

# CANADIAN JOURNAL OF RESEARCH

VOLUME 26

JUNE, 1948

NUMBER 6

## — SECTION B —

### CHEMICAL SCIENCES

#### *Contents*

	Page
A Study of Methods for the Extraction of Nitrogenous Material from Plants with Particular Reference to Subsequent Determination of the Lignin Content— <i>D. MacDougall and W. A. DeLong</i> - - - - -	457
A Study of the Effect of Reducing Conditions on the Amount and Nature of Lignin Isolable from Plants— <i>D. MacDougall and W. A. DeLong</i> - - - - -	464
A Method for the Determination of the Lignin Content of Fresh Plant Tissue without Preliminary Drying— <i>D. MacDougall and W. A. DeLong</i> - - - - -	468
The Effect of Added Vapors on the Inflammability of Hydrogen Cyanide— <i>K. J. McCallum and W. Graham</i> - - - - -	472
Aluminum Soaps as High Polymers— <i>H. Sheffer</i> - - - - -	481
Solid Solution Formation between Ammonium Nitrate and Potassium Nitrate— <i>John Whetstone</i> - - - - -	499

NATIONAL RESEARCH COUNCIL  
OTTAWA, CANADA

## CANADIAN JOURNAL OF RESEARCH

The *Canadian Journal of Research* is issued in six sections, as follows:

- |                       |                        |
|-----------------------|------------------------|
| A. Physical Sciences  | D. Zoological Sciences |
| B. Chemical Sciences  | E. Medical Sciences    |
| C. Botanical Sciences | F. Technology          |

For the present, Sections A, C, D, and E are to be issued six times annually, and Sections B and F, twelve times annually, each under separate cover, with separate pagination.

The *Canadian Journal of Research* is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. The *Canadian Journal of Research* is edited by a joint Editorial Board consisting of members of the National Research Council of Canada, the Royal Society of Canada, and the Chemical Institute of Canada.

Sections B and F of the *Canadian Journal of Research* have been chosen by the Chemical Institute of Canada as its medium of publication for scientific papers.

### EDITORIAL BOARD

<i>Representing</i> NATIONAL RESEARCH COUNCIL	<i>Representing</i> ROYAL SOCIETY OF CANADA	
DR. A. R. GORDON, ( <i>Chairman</i> ), Head, Department of Chemistry, University of Toronto, Toronto.	DR. A. NORMAN SHAW, Chairman, Department of Physics McGill University, Montreal.	} Section III
DR. C. H. BEST, The Banting and Best Department of Medical Research, University of Toronto, Toronto.	DR. J. W. T. SPINKS, Department of Chemistry, University of Saskatchewan, Saskatoon.	}
DR. ROBERT NEWTON, President, University of Alberta, Edmonton, Alta.	DR. E. HORNE CRAIGIE, Department of Zoology, University of Toronto, Toronto.	} Section V
DR. G. H. HENDERSON, Professor of Mathematical Physics, Dalhousie University, Halifax.	DR. H. S. JACKSON, Head, Department of Botany, University of Toronto, Toronto.	}
<i>Ex officio</i>	<i>Representing</i> THE CHEMICAL INSTITUTE OF CANADA	
DR. LÉO MARION, Editor-in-Chief, Division of Chemistry, National Research Laboratories, Ottawa.	DR. R. V. V. NICHOLLS, Associate Professor of Chemistry, McGill University, Montreal.	
DR. H. H. SAUNDERSON, Director, Division of Information Services, National Research Laboratories, Ottawa.		

### EDITORIAL COMMITTEE

Editor-in-Chief,	DR. LÉO MARION	Editor, Section D,	DR. E. HORNE CRAIGIE
Editor, Section A,	DR. A. NORMAN SHAW	Editor, Section E,	DR. J. B. COLLIP
Editor, Section B,	DR. J. W. T. SPINKS		DR. J. A. ANDERSON
	DR. R. V. V. NICHOLLS	Editor, Section F,	DR. R. V. V. NICHOLLS
Editor, Section C,	DR. H. S. JACKSON		DR. A. NORMAN SHAW

Manuscripts should be addressed:

*Editor-in-Chief,  
Canadian Journal of Research,  
National Research Council, Ottawa, Canada.*

# Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 26, SEC. B.

JUNE, 1948

NUMBER 6

## A STUDY OF METHODS FOR THE EXTRACTION OF NITROGENOUS MATERIAL FROM PLANTS WITH PARTICULAR REFERENCE TO SUBSEQUENT DETERMINATION OF THE LIGNIN CONTENT<sup>1</sup>

By D. MACDOUGALL<sup>2</sup> AND W. A. DELONG

### Abstract

A study has been made of methods for the removal of nitrogenous constituents from plant tissues prior to determination of their lignin contents. It was found that substitution of a continuous extraction method for the usual treatment with hot 1% hydrochloric acid had little effect on the amount of lignin isolated but apparently lowered its methoxyl content. Continuous extraction thus appears to cause some demethoxylation of lignin. Treatment with cold 5% acetic acid apparently can be substituted for the hot 1% hydrochloric acid extraction with very young but not with older, undried tissue. Ether saturated water was found to be the most satisfactory nonacid extractant for removal of nitrogen-containing material from young undried tissues. Upwards of 90% of the original nitrogen can be removed from such material by three extractions with this solvent. With older tissues or with material that has been dried, this proportion of the nitrogen cannot be removed except by extraction with hot dilute mineral acid.

### Introduction

Although modern theories of the structure of lignin make no provision for the inclusion of nitrogen in its molecule no one has ever succeeded in isolating nitrogen-free lignin from succulent plant tissues. The possibility that nitrogen is a fundamental component of the lignin of succulent plant tissues but not of wood lignin remains open. Most workers in the field (6, 7, 8) believe that the nitrogen in isolated plant lignin is of protein, or, at least, non-lignin origin, and is condensed with the lignin in the pretreatment or isolation procedures. Norman (6) states that the main disturbance is due to the condensation of relatively large protein fragments with the lignin, and that the interference due to simple amino acids is of a much smaller order. He also concludes that lignin has only a limited power to combine with such nitrogenous materials.

The removal of nitrogenous material from plant tissue prior to the final lignin determination has been studied by several workers. Norman (6) found

<sup>1</sup> Manuscript received in original form July 30, 1947, and as revised, March 13, 1948.

Contribution from the Faculty of Agriculture of McGill University, Macdonald College, Quebec, Canada. From part of a thesis by D. MacDougall presented to the Faculty of Graduate Studies and Research, McGill University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Macdonald College Journal Series No. 232.

<sup>2</sup> Holder of a studentship 1942-43 and a fellowship 1943-44 under the National Research Council of Canada. Present address:—Ontario Agricultural College, Guelph, Canada.

that successive short-time extractions with 5% sulphuric acid gave lignin yields from straw and oak wood that were lower than if one continuous hydrolysis were given. The decrease in apparent lignin content due to preliminary acid extraction may be due to more efficient removal of interfering material or to increased solution of lignin. Cohen and Harris (2) claimed that extraction with hot dilute mineral acid results in the removal of the more soluble part of the lignin. However, it is generally assumed that the interference avoided by use of the acid pretreatment is greater than any caused by solution of part of the lignin.

In the studies described in this paper, methods of removal of interfering nitrogenous material from succulent plant tissue have been investigated. Continuous extraction with hot 1% hydrochloric acid has been compared with the usual refluxing method. In a second set of experiments the mineral acid was replaced by 5% acetic acid. It was thought that the weak organic acid might have less effect on the lignin, but, at the same time, be as efficient as hydrochloric acid for the removal of nitrogenous material. A study also was made of the efficiency of certain protein extractants for the removal of nitrogen from succulent plant tissue.

### Experimental Methods and Results

The final lignin determinations for all experiments described in this paper were carried out by the 72% sulphuric acid method (5). Methods used for nitrogen and methoxyl determinations are described elsewhere (4).

#### CONTINUOUS ACID EXTRACTION

In view of the results of Norman (6) it was decided to investigate continuous extraction with 1% hydrochloric acid. Accordingly, an apparatus was set up for this purpose (see Fig. 1).

In this apparatus 1% hydrochloric acid was kept refluxing in a large flask, *B*. The hot acid flowed through a siphon into the bottom of the extractor, *A*. Thence the acid diffused up through alundum crucibles containing the samples. As the acid diffused out of the upper portion of the crucibles it was drawn off to a constant level, and a continuous extraction with hot 1% hydrochloric acid was thus obtained. The extractor, *A*, was placed in a boiling water bath, *C*.

The continuous extraction technique was used on young oat plants harvested 59 days after seeding. The plants were cut into  $\frac{1}{8}$  to  $\frac{1}{4}$  in. lengths and 10-gm. samples were weighed out. Each sample then received two half-hour extractions with 300 ml. of ethyl ether saturated water in the Waring Blendor, a three hour treatment with hot 1% hydrochloric acid in the extraction apparatus described, a two to three hour extraction with 95% ethanol in a Soxhlet to remove the water, and finally a 30 hr. Soxhlet extraction with ethanol-benzene (1 : 2). The technique was repeated using the usual refluxing method



(1) instead of the continuous acid extraction. Samples were also air-dried at room temperature and pretreated according to the official A.O.A.C. method (1).

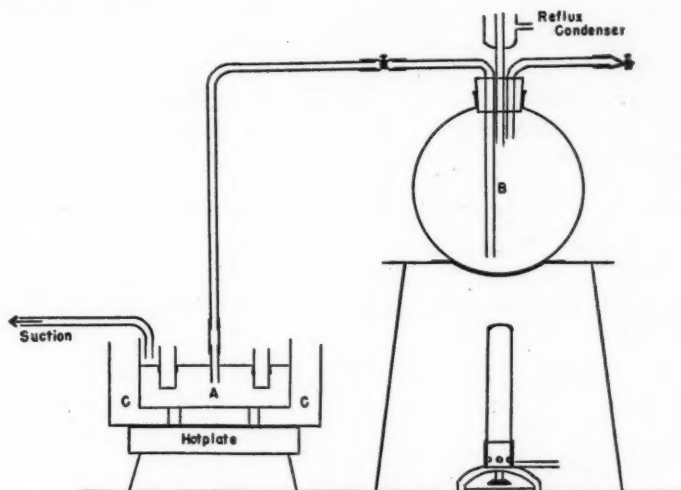


FIG. 1. Continuous extraction apparatus for 1% hydrochloric acid.

The apparent lignin contents of the materials described are shown in Table I. The pretreatment procedures are summarized in the table.

TABLE I

COMPARISON OF THE YIELDS AND ANALYTICAL CONSTANTS OF LIGNIN FRACTIONS ISOLATED FOLLOWING (a) CONTINUOUS EXTRACTION AND (b) REFLUXING WITH DILUTE HYDROCHLORIC ACID

Material	Pretreatment procedure	Lignin, %	Methoxyl in lignin, %	Nitrogen in lignin, %
Immature oat plants	1	$2.90 \pm 0.09$ (4)*	$2.75 \pm 0.01$ (2)	$1.98 \pm 0.01$ (2)
	2	$2.90 \pm 0.35$ (6)	$4.53 \pm 0.08$ (2)	$2.70 \pm 0.03$ (3)
	3	$3.68 \pm 0.11$ (2)	$7.18 \pm 0.04$ (3)	$4.29 \pm 0.05$ (3)

\* Each result is followed by the average deviation and, in parentheses, by the number of determinations carried out.

- Two half-hour extractions of fresh material with ether-water; three hour continuous extraction with 1% hydrochloric acid; 30 hr. Soxhlet extraction with ethanol-benzene.
- Similar to Pretreatment 1 except that sample was refluxed for three hours with 1% hydrochloric acid.
- Standard pretreatment. Air-dried material given 30 hr. Soxhlet extraction with ethanol-benzene, three hour refluxing with hot water, three hour refluxing with 1% hydrochloric acid.

Comparison of the results obtained by pretreatment procedures 1 and 2 shows that continuous extraction has little effect on the absolute amount of lignin isolated. The nitrogen results indicate that more interfering nitrogenous material is removed by continuous extraction than by the refluxing method. However, it also appears that continuous extraction causes some demethoxylation of lignin. In this connection Harris and Mitchell (3) have shown that treatment with mineral acids tends to lower the methoxyl content of lignin. Procedures 1 and 2 both gave less lignin which contained less methoxyl and less nitrogen than was obtained by the standard method.

#### MODIFICATION OF THE PROCEDURE TO AVOID THE USE OF MINERAL ACID

The advisability of using mineral acid for the pretreatment of materials on which the lignin content is to be determined has been questioned (2, 3). Accordingly it was decided to prepare material without the use of strong mineral acid.

In this study freshly harvested oat plants grown in both greenhouse and field were used. The greenhouse plants were cut at two growth stages. Hydrolysis with hot 1% hydrochloric acid was replaced by a treatment in the Waring Blendor with 5% acetic acid. The results were compared with the standard treatment (1) on air-dry material. In the case of the field grown oats, a determination was also carried out by the procedure for fresh material (4). In cases where fresh material was analyzed, a 75 gm. sample was extracted in the Waring Blendor for half an hour with 500 ml. of the appropriate extractant. The results are contained in Table II and the details of the procedures used are summarized in footnotes to the table. The ether-water was distilled water saturated with ethyl ether. The ethanol-benzene was constant boiling 1 : 2 mixture.

The results on greenhouse material indicate that the acetic acid method is just as efficient as the standard method for young tissue. This was also true in general for the field-grown plants. The differences between the lignin values for pretreatment procedures I, III, and IV on field-grown material are probably not significant. Lignin isolated by use of acetic acid (III, IV) contained more methoxyl and possibly less nitrogen than that obtained by the standard method (I), although the reverse is true when comparison is made with the results obtained by Method II, which is that outlined for fresh material (4).

The absolute methoxyl content of the lignin obtained by Treatments III and IV is considerably greater than of that obtained by Methods I and II on the same material. This may be due to inclusion in the lignin of methoxyl-containing carbohydrates, or to removal of a soluble fraction of the lignin in the hot mineral acid extraction. It is also possible, as suggested in connection with the continuous acid treatment, that mineral acid extraction demethoxylates the lignin to some extent.

TABLE II

COMPARISON OF YIELDS AND ANALYTICAL CONSTANTS OF LIGNIN FRACTIONS OBTAINED WHEN ACETIC ACID AND HYDROCHLORIC ACID ARE USED FOR THE HYDROLYTIC REMOVAL OF NON-LIGNIN COMPONENTS FROM OAT PLANTS

Source	Age, days	Pretreatment procedure	Lignin, %	Methoxyl in lignin, %	Nitrogen in lignin, %
Greenhouse	32	I	$3.57 \pm 0.13$ (3)*	$4.25 \pm 0.12$ (3)	$5.84 \pm 0.05$ (3)
		III	$3.27 \pm 0.54$ (7)	$5.08 \pm 0.01$ (3)	$5.03 \pm 0.01$ (2)
	140	I	$6.05 \pm 0.01$ (3)	$13.37 \pm 0.23$ (3)	$2.66 \pm 0.11$ (3)
		III	$11.61 \pm 0.14$ (3)	$11.84 \pm 0.32$ (3)	$2.20 \pm 0.06$ (3)
Field	27	I	$2.97 \pm 0.10$ (4)	$4.71 \pm 0.02$ (2)	$6.98 \pm 0.40$ (3)
		II	$1.51 \pm 0.16$ (3)	$8.29 \pm 0.30$ (3)	$3.08 \pm 0.01$ (2)
		III	$3.82 \pm 0.52$ (6)	$5.94 \pm 0.05$ (2)	$5.58 \pm 0.62$ (2)
		IV	$2.59 \pm 0.09$ (4)	$8.22 \pm 0.18$ (3)	$5.73 \pm 0.26$ (3)

\* Each value is followed by the average deviation and, in parentheses by the number of determinations carried out.

- I. Standard pretreatment. Air-dried material given 30 hr. Soxhlet extraction with ethanol-benzene; three hour refluxing with hot water; three hour refluxing with 1% hydrochloric acid.
- II. Fresh material given three ether-water extractions in Blendor, three hour refluxing with 1% hydrochloric acid; 30 hr. Soxhlet extraction with ethanol-benzene.
- III. Fresh material given one extraction with 5% acetic acid in Blendor; two extractions with ethanol-benzene in Blendor.
- IV. Fresh material given two extractions with ether-water in Blendor; one extraction with 5% acetic acid in Blendor; two extractions with ethanol-benzene in Blendor.

With the 140-day-old greenhouse material, a much higher lignin value was obtained by the acetic acid than by the standard method. The high methoxyl and relatively low nitrogen contents of the lignin obtained indicate that acetic acid is inefficient in removal of interfering carbohydrates from mature tissue.

It appears that the acetic acid method is satisfactory for young tissue and it effects a great saving in time and labor over the standard procedure. However, before it can be adopted, it will have to be modified for more efficient removal of interfering carbohydrates from mature material.

#### REMOVAL OF NITROGEN WITH VARIOUS PROTEIN EXTRACTANTS

This study was carried out on 27-, 34-, and 41-day-old freshly harvested oat plants. Air-dry material of the 27 day stage was also analyzed. Nitrogen contents of the original material and of the extracted residues were determined by the standard Kjeldahl method (1). Samples of fresh material (75 gm.) and of air-dry material (10 gm.) were weighed out for extraction.

The extractants used were ethyl ether saturated distilled water, 0.5 N sodium benzoate, distilled water, 1% hydrochloric acid, a 0.5 M sodium phosphate buffer, and ethanol-benzene, 1 : 2 constant boiling mixture. All

extractions except the 1% hydrochloric acid and the Soxhlet extraction with ethanol-benzene were carried out in the Waring Blendor for 30 min. The volume of extractant used in all Blendor extractions was 500 ml. The 1% hydrochloric acid extractions were carried out by refluxing for three hours (150 ml. per gm. dry weight). The Soxhlet extraction with ethanol-benzene was carried out for 30 hr.

The results of the experiments are contained in Table III. The numbers preceding the treatments refer to the number of extractions carried out.

TABLE III  
REMOVAL OF NITROGENOUS MATERIAL FROM OAT PLANTS OF VARIOUS  
AGES BY PROTEIN EXTRACTANTS

Age, days	Condition	Treatment	Nitrogen in original material, %	Percentage of original nitrogen in extracted material
27	Fresh	2 ether saturated water	4.41	16.6
		2 ether saturated water + 2 sodium benzoate	4.41	5.4
	Air-dry	3 ether saturated water	4.41	41.1
		3 ether saturated water + 2 ethanol-benzene	4.41	25.6
		3 ether saturated water + 2 ethanol-benzene + 1% hydrochloric acid	4.41	6.2
34	Fresh	3 ether saturated water	2.17	11.2
		3 ether saturated water + 2 ethanol-benzene	2.17	7.9
		3 water	2.17	18.0
		3 water + 2 ethanol-benzene	2.17	7.9
		3 phosphate buffer	2.17	12.7
		3 phosphate buffer + 2 ethanol-benzene	2.17	7.7
41	Fresh	3 ether saturated water + 2 ethanol-benzene	1.81	31.0
		3 ether saturated water + 1% hydrochloric acid + 30 hr. with ethanol-benzene in Soxhlet	1.81	4.4

The results of the experiments on young tissue show that 90 to 95% of the nitrogen can be removed from fresh material by cold Waring Blendor extractions without the use of acids. Sodium benzoate apparently removes a fraction not extractable with ether saturated water. It will be noted that the extractions were much less efficient with air-dry than with fresh tissue and, in the former case, treatment with hot 1% hydrochloric acid was necessary to remove a comparable amount of nitrogenous material.

The experiment on the 34-day-old plants indicates that ether-water and the phosphate buffer remove a portion of the nitrogen not extracted by distilled water. However, this substance is shown to be soluble in ethanol-benzene. Thus, when the ether-water is followed by ethanol-benzene extractions it has no advantage over either pure water or the phosphate

buffer. The material extracted with ether-water was filtered more easily than that treated with either of the other two reagents and, therefore, the use of the former was continued.

The results on 41-day-old tissue show that acid extraction is necessary to remove a proportion of the nitrogen comparable to that removed by nonacid extractants from the younger materials. Apparently increasing age brings about changes in protein solubility that are similar to those caused by drying of very young material.

### References

1. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Official and tentative methods of analysis. 5th ed. A.O.A.C., Washington, D.C. 1940.
2. COHEN, W. E. and HARRIS, E. E. Ind. Eng. Chem., Anal. Ed. 9 : 234. 1937.
3. HARRIS, E. E. and MITCHELL, R. L. Ind. Eng. Chem., Anal. Ed. 11 : 153. 1939.
4. MACDOUGALL, D. and DELONG, W. A. Can. J. Research B, 26 : 468. 1948.
5. MANNING, K. R. and DELONG, W. A. Sci. Agr. 22 : 69. 1941.
6. NORMAN, A. G. Biochem. J. 31 : 1567. 1937.
7. NORMAN, A. G. The biochemistry of cellulose, the polyuronides, lignin, etc. Oxford at the Clarendon Press. 1937.
8. NORMAN, A. G. and JENKINS, S. H. Biochem. J. 28 : 2160. 1934.



## A STUDY OF THE EFFECT OF REDUCING CONDITIONS ON THE AMOUNT AND NATURE OF LIGNIN ISOLABLE FROM PLANTS<sup>1</sup>

BY D. MACDOUGALL<sup>2</sup> AND W. A. DELONG

### Abstract

The effects of maintaining reducing conditions during both the pretreatment procedures and the final determination of lignin in plant tissues have been investigated. In studying the effects produced, consideration has been given, not only to the quantity of lignin obtained, but also to its quality as judged by its methoxyl and nitrogen contents. The introduction of hydrogen sulphide during the pretreatment procedures had little or no effect on the amount or the composition of the lignin fraction isolated from freshly harvested oat plants. With air-dried timothy, introduction of the hydrogen sulphide apparently prevented in a large measure the usual interference by nitrogen-containing substances. The presence of hypophosphorous acid in the 72% sulphuric acid had no effect on the final results. Constant boiling hydriodic acid was unsatisfactory as a substitute for 72% sulphuric acid in the final determination.

### Introduction

During the isolation of lignin from plant tissue, care must be taken to prevent changes in the lignin itself. As lignin is the most easily oxidized portion of the plant cell wall, changes occurring during its isolation are likely to be of an oxidative nature.

The oxidation of lignin was studied by Hibbert *et al.* (5) who showed that with increasing ozonization a decrease in methoxyl content and an increase in sodium bisulphite solubility are obtained. By alkaline oxidation of lignin sulphonic acids other workers have obtained vanillin (13), acetovanillone and guaiacol (8), syringaldehyde and 1,3-dimethoxypyrogallol (2), and acetosyringone (9). These workers believe that the products isolated result from breakdown of the lignin molecule. Similar products have been isolated from wood and claimed to be lignin precursors (3, 4).

Hägglund (6) pointed out the possibility that changes in the essential nature of lignin might take place during the isolation process. He claimed that an oxygen bridge was split, leaving free phenolic hydroxyl groups. He also mentions the possibility of condensation of other reactive plant substances with the liberated groups to give a high apparent lignin content.

In view of the possibility of such changes as Hägglund (6) suggests and the production, by oxidation of lignin, of reactive products such as Hibbert (7) has described, it seemed wise to undertake a study of the effect of reducing conditions on the lignin isolable from succulent plant tissues.

<sup>1</sup> Manuscript received in original form July 30, 1947, and, as revised, March 13, 1948.

Contribution from the Faculty of Agriculture of McGill University, Macdonald College, Que. From part of a thesis by D. MacDougall presented to the Faculty of Graduate Studies and Research, McGill University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Macdonald College Journal Series No. 233.

<sup>2</sup> Holder of a Studentship, 1942-43, and a Fellowship, 1943-44, under the National Research Council of Canada. Present address: Ontario Agricultural College, Guelph, Ont.

### Material and Methods

The materials used in this study included freshly harvested oat plants grown in the greenhouse and gathered at various growth stages, young field-grown timothy and young field-grown clover. The oat plants were not dried before analysis, while the timothy and clover were air-dried at room temperature and ground to pass a 40 mesh sieve.

Except where otherwise designated (see Table III, Treatments 3 and 4) the final lignin determinations were carried out by the 72% sulphuric acid method (12). The methods used for the nitrogen and methoxyl determinations are described elsewhere (11).

Pretreatment procedures included extractions in the Waring Blendor with ether saturated water for 30 min., refluxing with hot water for three hours, refluxing with 1% hydrochloric acid for three hours, and extraction in a Soxhlet for 30 hr. with ethanol-benzene (1 : 2). The technique for extraction of fresh material with ether saturated water has been described elsewhere (11). The ethanol-benzene, hot water, and 1% hydrochloric acid extractions were carried out as prescribed in the A.O.A.C. method (1). The pretreatment extractions given individual samples are summarized in footnotes to the tables.

The reducing agents investigated included hydrogen sulphide, 1% hydriodic acid, constant boiling hydriodic acid, and 10% hypophosphorous acid. Hydrogen sulphide was used in the determinations on oat plants and timothy, while the hydriodic and hypophosphorous acids were used on the clover. The methods of application of the various reducing agents are shown in the footnotes to the tables. After the pretreatments shown, samples that were treated with hydrogen sulphide received a four to five hour Soxhlet extraction with carbon tetrachloride to remove any precipitated sulphur. These were then dried in a vacuum desiccator in an atmosphere of nitrogen.

### Discussion of Results

The results of the experiments on oat plants, timothy, and clover are contained in Tables I, II, and III, respectively. All results are expressed on an oven-dry (105° C.) ash-free basis.

The results in Table I show that the hydrogen sulphide treatment had no consistent effect on either the quantity or quality of the lignin isolated from freshly harvested oat plants. In the case of the air-dried timothy the reducing agent apparently prevented inclusion in the lignin residue of a considerable portion of the nitrogen-containing material ordinarily present. As the bulk of the nitrogen originally present is removed by the extraction with 1% hydrochloric acid (10) the observed effect may have been due to increased efficiency of extraction at this stage. The possibility that the effect is partially due to the presence of the reducing agent during the ethanol-benzene extraction and the final extraction with 3% sulphuric acid must not be overlooked.

TABLE I

EFFECT OF HYDROGEN SULPHIDE TREATMENT DURING ISOLATION ON THE YIELD AND COMPOSITION OF LIGNIN ISOLABLE FROM UNDRIED OAT PLANTS

Age, days	Pretreatment procedure	Lignin, %	Methoxyl in lignin, %	Nitrogen in lignin, %
32	A	$2.62 \pm 0.18$ (4)*	$3.80 \pm 0.12$ (3)	$3.70 \pm 0.11$ (2)
	A + H <sub>2</sub> S	$2.24 \pm 0.08$ (4)	$5.07 \pm 0.01$ (3)	$4.47 \pm 0.05$ (2)
66	A	$2.89 \pm 0.02$ (2)	$8.56 \pm 0.17$ (3)	$2.92 \pm 0.02$ (2)
	A + H <sub>2</sub> S	$2.91 \pm 0.03$ (2)	$7.92 \pm 0.12$ (3)	$3.12 \pm 0.03$ (2)
80	A	$3.22 \pm 0.19$ (4)	$11.87 \pm 0.10$ (3)	$1.82 \pm 0.04$ (3)
	A + H <sub>2</sub> S	$3.47 \pm 0.11$ (4)	$12.70 \pm 0.11$ (3)	$1.49 \pm 0.03$ (3)
94	A	$4.82 \pm 0.05$ (2)	$13.10 \pm 0.17$ (3)	$1.52 \pm 0.01$ (3)
	A + H <sub>2</sub> S	$5.53 \pm 0.17$ (2)	$11.25 \pm 0.11$ (3)	$2.04 \pm 0.04$ (3)
140	A	$6.25 \pm 0.13$ (3)	$15.44 \pm 0.24$ (3)	$1.33 \pm 0.01$ (3)
	A + H <sub>2</sub> S	$6.85 \pm 0.10$ (3)	$14.48 \pm 0.03$ (3)	$1.12 \pm 0.06$ (3)

\* Each value is followed by the average deviation and, in parentheses, by the number of determinations performed.

A—Two extractions with ether saturated water in Waring Blendor; three hour refluxing with 1% hydrochloric acid; 30 hr. extraction in Soxhlet with ethanol-benzene (1:2).

A + H<sub>2</sub>S—Similar to Treatment A except that ether saturated water was saturated with hydrogen sulphide, hydrogen sulphide was passed through apparatus during 1% hydrochloric acid extraction, ethanol-benzene extraction, and treatment with 3% sulphuric acid in final isolation of lignin.

TABLE II

EFFECT OF HYDROGEN SULPHIDE TREATMENT DURING ISOLATION ON THE YIELD AND THE ANALYTICAL CONSTANTS OF LIGNIN FRACTIONS ISOLABLE FROM AIR-DRIED TIMOTHY PLANTS. (HARVESTED, MAY 29, 1942.)

Pretreatment procedure	Lignin, %	Methoxyl in lignin, %	Nitrogen in lignin, %
B B + H <sub>2</sub> S	$6.41 \pm 0.06$ (3)*	$7.39 \pm 0.15$ (3)	$4.24 \pm 0.06$ (2)
	$5.67 \pm 0.15$ (6)	$7.69 \pm 0.33$ (5)	$2.37 \pm 0.18$ (5)

\* Each value is followed by the average deviation and, in parentheses, by the number of determinations carried out.

B—Three hour refluxing with hot 1% hydrochloric acid; 30 hr. extraction in Soxhlet with ethanol-benzene (1:2).

B + H<sub>2</sub>S—Similar to Treatment B except that hydrogen sulphide was passed through apparatus during 1% hydrochloric acid extraction, ethanol-benzene extraction, and treatment with 3% sulphuric acid in final isolation of lignin.

The results of the experiments on clover are contained in Table III. Comparison of the results for Treatments 1 and 2 would seem to indicate that in spite of its reducing properties a 1% solution of hydriodic acid is somewhat less efficient for removal of interfering material than a 1% solution of hydrochloric acid. This is indicated by the higher lignin, lower methoxyl, and somewhat higher nitrogen value obtained by Treatment 2. The use of

TABLE III

EFFECT OF REDUCING CONDITIONS AT DIFFERENT STAGES IN THE ANALYSIS ON THE APPARENT LIGNIN CONTENT AND THE ANALYTICAL CONSTANTS OF LIGNIN FRACTIONS ISOLATED FROM YOUNG CLOVER PLANTS (HARVESTED, MAY 28, 1942.)

Treatment	Lignin, %	Methoxyl in lignin, %	Nitrogen in lignin, %
1	5.91 $\pm$ 0.06 (3)*	5.09 $\pm$ 0.09 (3)	6.16 $\pm$ 0.06 (3)
2	6.65 $\pm$ 0.15 (3)	3.78 $\pm$ 0.26 (2)	7.08 $\pm$ 0.41 (4)
3	18.80 $\pm$ 0.02 (2)	1.53 $\pm$ 0.01 (3)	2.65 $\pm$ 0.33 (3)
4	5.91 $\pm$ 0.15 (3)	4.87 $\pm$ 0.12 (3)	6.77 $\pm$ 0.15 (3)

\* Each value is followed by the average deviation and, in parentheses, by the number of determinations carried out.

1. Standard pretreatment—Extraction with ethanol-benzene (1:2) in Soxhlet for 30 hr.; refluxing with water for three hours and with 1% hydrochloric acid for three hours.

2. One per cent hydrochloric acid of Treatment 1 replaced by 1% hydriodic acid.

3. Standard pretreatment. Seventy-two per cent sulphuric acid in final determination replaced by constant boiling hydriodic acid.

4. Standard pretreatment. Seventy-two per cent sulphuric acid in final determination contained 10% hypophosphorous acid.

constant boiling hydriodic instead of 72% sulphuric acid (Treatment 4) resulted in a much larger residue than is ordinarily obtained. The absolute methoxyl content of the residue was about the same as that in the lignin isolated by the standard treatment, but the absolute nitrogen content was considerably higher. The latter observation indicates that a portion of the nonlignin material in the residue is of protein origin. Comparison of the results for Treatments 1 and 4 shows that addition of hypophosphorous acid to the 72% sulphuric acid had no significant effect on either the amount or composition of the lignin residue obtained.

### References

1. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Official and tentative methods of analysis. 5th ed. A.O.A.C., Washington, D.C. 1940.
2. BELL, A., HAWKINS, W. L., WRIGHT, G. F., and HIBBERT, H. J. Am. Chem. Soc. 59 : 598. 1937.
3. BRICKMAN, L., HAWKINS, W. L., and HIBBERT, H. J. Am. Chem. Soc. 62 : 2149. 1940.
4. BRICKMAN, L., PYLE, J. J., HAWKINS, W. L., and HIBBERT, H. J. Am. Chem. Soc. 62 : 986. 1940.
5. DORLAND, R. M., HAWKINS, W. L., and HIBBERT, H. J. Am. Chem. Soc. 61 : 2698. 1939.
6. HÄGGLUND, E. Zellstoff u. Papier 16 : 570. 1936. Abstracted in Chem. Abstracts, 31 : 2418. 1937.
7. HIBBERT, H. Ann. Rev. Biochem. 11 : 183. 1942.
8. LEGER, F. and HIBBERT, H. Can. J. Research, B, 16 : 68. 1938.
9. LEGER, F. and HIBBERT, H. J. Am. Chem. Soc. 60 : 565. 1938.
10. MACDOUGALL, D. and DELONG, W. A. Can. J. Research, B, 26 : 457. 1948.
11. MACDOUGALL, D. and DELONG, W. A. Can. J. Research, B, 26 : 468. 1948.
12. MANNING, K. R. and DELONG, W. A. Sci. Agr. 22 : 69. 1941.
13. TOMLINSON, G. H., 2nd, and HIBBERT, H. J. Am. Chem. Soc. 58 : 345. 1936.

## A METHOD FOR THE DETERMINATION OF THE LIGNIN CONTENT OF FRESH PLANT TISSUE WITHOUT PRELIMINARY DRYING<sup>1</sup>

By D. MacDOUGALL<sup>2</sup> AND W. A. DeLONG

### Abstract

A method of determining the lignin content of fresh plant tissue without preliminary drying has been devised. Prior to the final lignin determination with 72% sulphuric acid, the tissue is cut up, extracted with ether saturated water in a Waring Blendor, refluxed with 1% hydrochloric acid, and finally extracted with ethanol-benzene. For comparison, determinations were carried out by the above method and the standard A.O.A.C. procedure on material that had been air-dried at room temperature. Both greenhouse and field grown oat plants cut at various growth stages were used in this study. The modified method gave lower lignin values than the standard procedure with young succulent tissue. This difference decreased as the age of the tissue increased, and the results by all methods were very similar with oat straw. That the modified procedure on fresh tissue removes more interfering nitrogenous material than the other methods used is indicated by the lower nitrogen content of the lignin isolated. The absolute methoxyl contents of the residues isolated from dried tissue were greater than of those isolated from fresh material (from the same source). This may have been due to the inclusion of more methoxyl-containing carbohydrates in the former residues.

### Introduction

Recent work by the authors has emphasized the dangers of high temperature drying in the preparation of succulent plant tissues for analyses for lignin content (7). Turnips, young rye, silage, rhubarb, and beets were dried at room temperature and at 105° C. In some cases there was six times as much apparent lignin in the material dried at the high temperature.

Campbell and Booth (2, 3) found that oven-drying resulted in an increase in the apparent lignin content of both soft and hard woods. At the same time there was a corresponding decrease in furfuraldehyde-yielding material, suggestive of condensation of the latter with lignin.

Waksman and Iyer (13) report experiments in which protein was added to lignin preparations. They maintain that formation of a ligno-protein took place and that the resistance of such a complex to microbial decomposition was rendered greater by drying and by an elevated temperature of formation. It seems possible that similar complexes may be formed in succulent tissues on drying at an elevated temperature, or, if such complexes are previously formed, they may at least be rendered more resistant to subsequent decomposition.

<sup>1</sup> Manuscript received in original form July 30, 1947, and, as revised, March 13, 1948.

Contribution from the Faculty of Agriculture of McGill University, Macdonald College, Quebec, Canada. From part of a thesis by D. MacDougall presented to the Faculty of Graduate Studies and Research, McGill University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Macdonald College Journal Series No. 234.

<sup>2</sup> Holder of a Studentship, 1942-43, and a Fellowship, 1943-44, under the National Research Council of Canada. Present address: Ontario Agricultural College, Guelph, Canada.



In view of the errors known to be caused by high temperature drying and the ease of oxidation of lignin (11, p. 166), it was deemed advisable to attempt removal of the bulk of the interfering material from tissue before drying.

### Material and Methods

At the outset it was decided to break up the fresh plant material by use of the Waring Blendor. The standard A.O.A.C. procedure (1) involves successive extractions with ethanol-benzene (1 : 2), hot water, and hot 1% hydrochloric acid. However, as ethanol-benzene is immiscible with water, and fresh tissue contains 80 to 90% moisture, it was decided to change the usual order, giving the aqueous extractions first and the ethanol-benzene extraction after air drying at room temperature. A preliminary investigation (8) of removal of nitrogenous material from fresh plant tissue showed that ether saturated water was the most efficient extractant and this was adopted instead of water alone.

The procedure as finally adopted is as follows. A 75 gm. sample and a 20 gm. sample of fresh material are weighed out. These are cut into  $\frac{1}{4}$  to  $\frac{1}{8}$  in. lengths. The 20 gm. sample is dried at 105° C. while the 75 gm. sample is used for the lignin determination. The sample is placed in the Waring Blendor with 450 ml. of distilled water, and 50 ml. of ethyl ether is added. After extraction for 30 min. the residual material is separated by centrifuging. The extraction is repeated twice. The residue is then refluxed with 1% hydrochloric acid for three hours. One hundred and fifty milliliters are used for each gram of dry weight in the original sample. This volume must be estimated at this point. After filtering, the material is air-dried at room temperature and extracted in a Soxhlet with ethanol-benzene (1 : 2) for 30 hr. The final residue is used for the lignin determination.

The method was studied on oat plants of various growth stages. Both greenhouse and field grown oats were used. For the purpose of comparison, samples were air-dried at room temperature and portions of these were treated as outlined above and by the standard A.O.A.C. (1) extraction procedure.

All lignin determinations were carried out by the method of Manning and DeLong (9). Lignin for nitrogen and methoxyl determinations was isolated by filtering in sintered glass crucibles using naphthalene as filter-aid. This technique was originally described by Mueller and Herrmann (10). Nitrogen was determined by the micro-Kjeldahl method using the digestion mixture recommended by Campbell and Hanna (4). Methoxyl determinations were carried out by the Viebock and Schwappach modification of the Zeisel method as described by Clark (5). Samples were weighed out in gelatin capsules and a suspension of red phosphorus was used in the scrubber. These modifications were recommended by Samsel and McHard (12). The hydriodic acid was prepared as described by Clark (6).

The complete results of the experiment are contained in Table I. The pretreatment procedures are designated A, B, and standard, and are summarized in footnotes to the table.

TABLE I

YIELDS AND ANALYTICAL CONSTANTS OF LIGNIN FRACTIONS ISOLATED BY APPLICATION OF THE STANDARD AND MODIFIED PROCEDURES OF ANALYSIS TO OAT PLANTS DIFFERING IN ORIGIN AND IN STAGE OF MATURITY

Origin	Age, days	Pretreatment procedures	Lignin, %	Methoxyl in lignin, %	Nitrogen in lignin, %
Plants grown in greenhouse	32	A	$2.62 \pm 0.18$ (4)*	$3.80 \pm 0.12$ (3)	$3.70 \pm 0.10$ (2)
		Standard	$3.57 \pm 0.13$ (3)	$4.25 \pm 0.15$ (3)	$5.84 \pm 0.05$ (3)
	59	A	$2.90 \pm 0.35$ (6)	$4.53 \pm 0.08$ (2)	$2.70 \pm 0.03$ (2)
		Standard	$3.68 \pm 0.11$ (2)	$7.18 \pm 0.04$ (3)	$4.29 \pm 0.05$ (3)
Plants grown in field	94	A	$4.85 \pm 0.05$ (2)	$13.01 \pm 0.17$ (3)	$1.52 \pm 0.01$ (3)
		Standard	$6.67 \pm 0.04$ (3)	$11.47 \pm 0.15$ (3)	$2.56 \pm 0.08$ (3)
	140	A	$6.25 \pm 0.01$ (3)	$15.44 \pm 0.24$ (3)	$1.33 \pm 0.01$ (2)
		Standard	$6.05 \pm 0.01$ (3)	$13.37 \pm 0.23$ (3)	$2.66 \pm 0.11$ (3)
	27	A	$1.51 \pm 0.16$ (3)	$8.29 \pm 0.30$ (3)	$3.08 \pm 0.01$ (2)
		B	$2.28 \pm 0.14$ (3)	$6.16 \pm 0.16$ (3)	$4.71 \pm 0.11$ (3)
		Standard	$2.97 \pm 0.10$ (4)	$4.71 \pm 0.02$ (2)	$6.98 \pm 0.40$ (3)
	34	B	$1.91 \pm 0.12$ (3)	$9.13 \pm 0.20$ (3)	$2.61 \pm 0.15$ (3)
		Standard	$3.93 \pm 0.04$ (3)	$10.18 \pm 0.55$ (3)	$3.46 \pm 0.04$ (3)
	41	A	$4.77 \pm 0.15$ (5)	$12.66 \pm 0.13$ (3)	$1.50 \pm 0.02$ (3)
		B	$5.51 \pm 0.02$ (3)	$13.42 \pm 0.15$ (3)	$2.04 \pm 0.03$ (2)
		Standard	$6.81 \pm 0.10$ (3)	$13.28 \pm 0.14$ (3)	$2.34 \pm 0.15$ (3)
	56	A	$5.62 \pm 0.13$ (6)	$14.59 \pm 0.13$ (3)	$1.82 \pm 0.15$ (3)
		B	$6.14 \pm 0.14$ (3)	$14.43 \pm 0.15$ (3)	$1.36 \pm 0.05$ (2)
		Standard	$6.90 \pm 0.05$ (3)	$13.22 \pm 0.59$ (2)	$2.71 \pm 0.03$ (2)
	75	A	$10.88 \pm 0.11$ (8)	$15.34 \pm 0.28$ (4)	$0.48 \pm 0.04$ (4)
		B	$9.91 \pm 0.18$ (3)	$16.32 \pm 0.37$ (3)	$0.96 \pm 0.04$ (2)
		Standard	$10.61 \pm 0.19$ (3)	$14.88 \pm 0.23$ (3)	$1.22 \pm 0.04$ (2)

\* Each value is followed by the average deviation and, in parentheses, by the number of determinations performed.

A. Three extractions of fresh material in Waring Blendor with ether saturated water; three hour refluxing with 1% hydrochloric acid; 30 hr. extraction in Soxhlet with ethanol-benzene.

B. Similar to Treatment A but carried out on material dried at room temperature.

Standard—Material dried at room temperature; extracted for 30 hr. in Soxhlet with ethanol-benzene; refluxed for three hours with water; refluxed for three hours with 1% hydrochloric acid.

### Discussion of Results

From the results obtained, it is evident that the modified procedure gives a lower apparent lignin content for young succulent tissue than the standard method. The difference in results decreases as the age of the tissue from which the lignin is being isolated increases. In every case, lignin isolated by the modified procedure contains less nitrogen than that isolated by the standard method. It appears, therefore, that the interference by nitrogenous compounds has been decreased. Comparison of the methoxyl results shows that the absolute amount of methoxyl isolated by the standard method is greater than that isolated by the modified procedure, except in the case of

mature tissue. It appears that there is less interference by methoxyl-containing carbohydrates in the modified method.

The results on the field grown oat plants show that approximately 50% of the difference in the results obtained by the two methods is due to modification of the pretreatment procedures and not to the fact that material for the standard method was dried. The main difference between the two procedures is that the acid treatment is preceded in one case by cold ether-water extractions and in the other by a hot water extraction. It would appear either that the ether-water treatments remove material not removed by the hot water extraction, or that the hot water causes condensation reactions that prevent removal of a portion of the interfering material by the subsequent hot acid treatment.

It should be noted that the greenhouse plants contained less lignin than those grown in the field and cut at the same age. This was likely due to the slower rate of maturing in the greenhouse. It appears that 94-day-old greenhouse plants were at about the same stage of maturity as 41-day-old plants from the field.

The results indicate that lignin values obtained with young tissue by the modified procedure are more reliable than those obtained by the standard method. The nitrogen results, in particular, indicate that lignin isolated from fresh tissue by the modified method is less contaminated than is that isolated by the standard procedure. For mature tissue in which the amount of possible interfering materials is relatively low, the standard procedure appears to give quite reliable results.

### References

1. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Official and tentative methods of analysis. 5th ed. A.O.A.C., Washington, D.C. 1940.
2. CAMPBELL, W. G. and BOOTH, J. *Biochem. J.* 24 : 641. 1930.
3. CAMPBELL, W. G. and BOOTH, J. *Biochem. J.* 25 : 756. 1931.
4. CAMPBELL, W. R. and HANNA, M. I. *J. Biol. Chem.* 119 : 1. 1937.
5. CLARK, E. P. *J. Assoc. Official Agr. Chem.* 15 : 136. 1932.
6. CLARK, E. P. *Ind. Eng. Chem., Anal. Ed.* 10 : 677. 1938.
7. MACDOUGALL, D. and DELONG, W. A. *Can. J. Research, B*, 20 : 40. 1942.
8. MACDOUGALL, D. and DELONG, W. A. *Can. J. Research, B*, 26 : 457. 1948.
9. MANNING, K. R. and DELONG, W. A. *Sci. Agr.* 22 : 69. 1941.
10. MUELLER, W. J. and HERRMANN, W. *Tech.-Wiss. Teil, Papierfabr.* 24 : 185. 1926. *Abstracted in Chem. Abstracts*, 20 : 2746. 1926.
11. NORMAN, A. G. *The biochemistry of cellulose, the polyuronides, lignin, etc.* Oxford at the Clarendon Press. 1937.
12. SAMSEL, E. P. and MCHARD, J. A. *Ind. Eng. Chem., Anal. Ed.* 14 : 750. 1942.
13. WAKSMAN, S. A. and IYER, K. R. N. *Soil Sci.* 36 : 69. 1933.

## THE EFFECT OF ADDED VAPORS ON THE INFLAMMABILITY OF HYDROGEN CYANIDE<sup>1</sup>

BY K. J. MCCALLUM AND W. GRAHAM<sup>2</sup>

### Abstract

The limits of inflammability of hydrogen cyanide - air mixtures at room temperature and approximately 1 atm. pressure, have been determined to be 7.8 and 42.4 volume % of hydrogen cyanide. The effect of the addition of cyanogen chloride, phosgene, chloroform, hexane, heptane, and methyl chloroformate upon these limits has been investigated. It was found that the minimum molar ratio of added vapor to hydrogen cyanide that will produce a mixture that never becomes inflammable when progressively diluted with air is equal to 4.7 for cyanogen chloride, 0.86 for phosgene, and 1.1 for chloroform. All mixtures of hexane, heptane, and methyl chloroformate with hydrogen cyanide become inflammable when suitably diluted with air. For these systems, Le Chatelier's law, dealing with the composition of limit mixtures of two inflammable gases with air, was found to hold.

### Introduction

The inflammability limits of hydrocyanic acid vapor in air have been reported by several investigators but the results are not in close agreement. Jorissen (5) in 1928 reported the limits to be 12.75 and 27.0 mole % of hydrogen cyanide. These results were not confirmed by Peters and Ganter (8) who obtained the values 7.0 and 41.0 volume %. In addition, two other values of the lower limit have been reported, namely, 8 volume % by Bohman (1) and 7.2 volume % by Stusiak and Seyer (10).

In this paper are reported the results of a redetermination of the inflammability limits of hydrogen cyanide in air, as well as the effect on these limits of the addition of other vapors. The substances whose effect was investigated were cyanogen chloride, phosgene, chloroform, hexane, heptane, and methyl chloroformate.

### Apparatus and Procedure

Gas mixtures were tested for inflammability in a Pyrex tube 47.5 mm. inside diameter and 103 cm. long. Previous investigations (2) have shown that, in general, an increase in the dimensions of the inflammability tube above these values has only a small effect on the measured inflammability limits of gaseous systems.

Tungsten electrodes with a spark gap of 1.5 mm. were sealed in at the bottom of the tube, which was closed with a hollow ground-glass stopper. Inside the tube was placed a small cylindrical mixer made from two circular plates of transite separated by glass pins. When not in use, the mixer could

<sup>1</sup> Manuscript received February 3, 1948.

<sup>2</sup> Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

<sup>3</sup> Holder of a Bursary under the National Research Council of Canada.

be suspended from a small indentation at the upper end of the tube. This end was connected through a stopcock and rubber pressure tubing to a capillary manifold for the introduction of gases.

The capillary manifold was connected to drying tubes containing anhydrous calcium chloride, through which air could be admitted to the apparatus or the manifold could be evacuated. Small tubes were connected to the manifold by stopcocks through which vapors of the materials under investigation could be admitted independently into the apparatus. A mercury manometer was attached for the measurement of the partial pressures of the gases in the inflammability tube.

For the preparation of a vapor mixture, the tube, manometer, and manifold were first evacuated, and then the vapors admitted separately to the apparatus, the total pressure being measured after the introduction of each vapor. Finally, air was admitted until the total pressure reached atmospheric. The inflammability tube was then disconnected from the manifold and the vapors were mixed by inverting the tube so that the mixer passed up and down the tube 60 times. Experiments using known mixtures of oxygen and nitrogen in the tube with this method of mixing indicated that 50 passes of the mixer were sufficient to ensure homogeneity of the mixture within the accuracy of the gas analysis.

The tube was then clamped in a vertical position with the mixer suspended at the top. The ground-glass stopper at the bottom was removed and the mixture tested for inflammability by passing a small flame across the open end or by passing a spark between the electrodes. The mixture was not recorded as inflammable unless the flame was propagated upwards the whole length of the tube. This procedure was repeated, the partial pressure of the vapors being varied until mixtures were found that were approximately 0.15% on either side of the limit mixture.

All observations were made with upward propagation of the flame and with the lower end of the tube open.

### Materials

Commercial grade liquid hydrocyanic acid was dried with anhydrous calcium chloride. The vapors were analyzed by maintaining the liquid at room temperature and collecting successive portions of the vapor by condensation in small glass bulbs cooled in a dry ice-acetone bath. After the bulbs were sealed and weighed, they were broken under sodium hydroxide solution. The solution was then neutralized and titrated with standard silver nitrate solution using potassium iodide in ammonium hydroxide as indicator (11). The experimental values found were 100.4% HCN (100.3, 100.6) on the first fraction of the vapor and 100.4% (100.2, 100.6) on the final fraction.

Commercial grade cyanogen chloride was distilled and further purified by the method of Douglas and Winkler (3). Small samples of the liquid were volatilized and the condensate analyzed. The analysis indicated 100.1%



CNCI (100.1, 100.2). A determination of the amount of hydrogen cyanide by the silver nitrate titration showed 0.0% HCN.

Commercial grade phosgene was used as received, with no further purification. The percentage of free chlorine in the material was determined by the method of Nenitzescu and Pana (7) to be 0.46%. No attempt was made to determine carbon monoxide or other gases.

The hexane and heptane were Eastman Kodak Company products from petroleum. The values of the refractive index at 20° C., using the sodium D line, were 1.37576 and 1.39842, respectively, as compared with the values 1.37506 and 1.39774 given by Egloff (4).

The chloroform was Merck's technical grade with a refractive index at 20° C. for the sodium D line of 1.44517. The value given in the International Critical Tables is 1.44482.

The methyl chloroformate was prepared by the reaction between phosgene and methyl alcohol using the method given by Sartori (9). The crude product was washed with ice-water, dried over anhydrous calcium chloride, and fractionally distilled, the fraction boiling in the range 70° to 72° C. being collected. This fraction was analyzed by decomposing a known weight in 0.5 *N* sodium hydroxide and determining the resultant chloride by the Fajans method. This analysis indicated 99.75% (99.72, 99.78) methyl chloroformate.

### Results

A preliminary series of inflammability tests on mixtures of hydrogen cyanide, cyanogen chloride, and air were made using as the source of ignition the spark from a Ford induction coil with a 6 v. primary. It was noticed that mixtures near the lower limit, which could not be ignited with this spark, were inflammable when tested with a small flame. Increasing the primary voltage applied to the induction coil caused a decrease in the experimental value of the lower inflammability limit, until, above 20 v., no further decrease was noted. At this voltage the inflammability limits coincided with those obtained using a small gas flame as the source of ignition. Since the inflammability limit of a gaseous mixture should describe the ability of the mixture to propagate flame and not the ability of the source to initiate combustion, all inflammability tests in the experiments reported here were made with a flame as source of ignition.

In Table I are given the inflammability limits on mixtures of hydrogen cyanide, cyanogen chloride, and air. In Columns 1 and 2 are given the partial pressure of hydrogen cyanide and cyanogen chloride, respectively, between which the limits were found to lie. The last three columns give the volume per cent of hydrogen cyanide, cyanogen chloride, and air in the limit mixtures calculated on the assumption that partial pressure per cent is equal to volume per cent for these vapors.

Similar results are given for the systems hydrogen cyanide - phosgene - air and hydrogen cyanide - chloroform - air in Tables II and III, respectively.

TABLE I

LIMITS OF INFLAMMABILITY FOR HYDROGEN CYANIDE - CYANOGEN CHLORIDE - AIR

Partial pressure of limit mixtures, mm. mercury		Barometer height, mm. mercury	Vol. % HCN Mean	Vol. % CNCI Mean	Vol. % Air Mean
HCN	CNCI				
54.7 - 55.2	0	707.0	7.8	0	92.2
37.7 - 39.0	149.9	711.0	5.3	21.1	73.6
37.5 - 38.4	180.0 - 181.1	719.2	5.3	25.1	69.6
42.4 - 43.8	125.1	719.2	6.0	17.4	76.6
46.3 - 47.3	69.9	711.3	6.6	9.8	83.6
46.4 - 48.0	100.0	711.7	6.6	14.1	79.3
48.0 - 48.1	199.9 - 201.7	714.1	6.7	28.1	65.2
49.4 - 50.1	49.6 - 50.4	713.6	7.0	7.0	86.0
55.1	209.5 - 211.0	714.6	7.7	29.4	62.9
65.8	218.8 - 220.2	722.8	9.1	30.4	60.5
72.3 - 72.4	223.1 - 221.5	722.7	10.1	30.8	59.1
79.8 - 79.9	223.0 - 221.8	722.7	11.1	30.8	58.1
86.9 - 87.0	222.1 - 224.2	716.0	12.1	31.2	56.7
92.9	222.1 - 223.7	715.8	13.0	31.1	55.9
101.2	224.2 - 226.1	718.0	14.1	31.4	54.5
120.0	216.1 - 218.0	715.5	16.8	30.3	52.9
133.4	207.8 - 209.2	714.6	18.9	29.5	51.6
150.0	200.8 - 202.7	715.5	21.0	28.2	50.8
200.1	152.3 - 154.8	715.5	28.0	21.4	50.6
253.9 - 254.0	69.8 - 72.2	715.5	35.5	9.9	54.6
299.0 - 299.7	0	706.0	42.4	0	57.6

TABLE II

INFLAMMABILITY LIMITS FOR HYDROGEN CYANIDE - PHOSGENE - AIR

Partial pressure of limit mixtures, mm. mercury		Barometer height, mm. mercury	Vol. % HCN Mean	Vol. % COCl <sub>2</sub> Mean	Vol. % Air Mean
HCN	COCl <sub>2</sub>				
54.7 - 55.2	0	707.0	7.8	0	92.2
71.2 - 71.7	16.2 - 18.2	710.1	10.1	2.4	87.5
79.7 - 82.5	36.4	718.0	11.3	5.1	83.6
86.8	60.1 - 62.0	714.3	12.1	8.6	79.3
99.8	84.7 - 89.2	716.2	13.9	12.1	74.0
125.0	100.6 - 100.2	722.3	17.3	14.1	68.6
149.8 - 150.3	106.8 - 108.4	712.3	21.1	15.1	63.8
175.0	108.2 - 109.9	722.3	24.2	15.1	60.7
200.0	96.8 - 99.7	710.0	28.2	13.9	57.9
224.8	90.0 - 92.5	722.3	31.1	12.6	56.3
250.0 - 250.5	72.1 - 73.0	722.6	34.6	10.0	55.4
275.1	43.8 - 45.9	722.3	38.1	6.2	55.7
299.0 - 299.7	0	706.0	42.4	0	52.6

The effect of the addition of hexane, heptane, and methyl chloroformate is shown in Tables IV, V, and VI. These vapors are themselves inflammable in air. It was noted that the upper limit mixtures formed with hexane and heptane burned with a very faint flame, so that it was necessary to make observations in the dark.

TABLE III  
INFLAMMABILITY LIMITS FOR HYDROGEN CYANIDE - CHLOROFORM - AIR

Partial pressure of limit mixtures, mm. mercury		Barometer height, mm. mercury	Vol. % HCN Mean	Vol. % CHCl <sub>3</sub> Mean	Vol. % Air Mean
HCN	CHCl <sub>3</sub>				
54.7 - 55.2	0	707.0	7.8	0	92.2
86.3	83.3 - 84.6	720.0	12.0	11.7	76.3
100.3	105.3 - 110.3	716.4	14.0	15.0	71.0
115.3	113.9 - 116.7	719.2	16.0	16.0	68.0
171.1	96.0 - 100.0	720.0	23.8	13.7	62.5
220.4	66.8 - 71.7	713.0	30.9	9.7	59.4
299.0 - 299.7	0	706.0	42.4	0	57.6

TABLE IV  
INFLAMMABILITY LIMITS FOR HYDROGEN CYANIDE - HEXANE - AIR

Partial pressure of limit mixtures, mm. mercury		Barometer height, mm. mercury	Vol. % HCN Mean	Vol. % Hexane Mean	Vol. % Air Mean
HCN	Hexane				
54.7 - 55.2	0	707.0	7.8	0	92.2
14.5 - 16.6	7.8 - 8.2	727.8	2.1	1.1	96.8
25.0 - 26.9	6.1 - 6.6	727.8	3.6	0.9	95.5
50.0	42.2 - 43.5	721.5	6.9	5.9	87.2
100.0	33.9 - 35.6	721.5	13.9	4.8	81.3
150.0	21.9 - 23.4	719.7	20.9	3.2	75.9
200.4	15.5 - 16.0	721.5	27.8	2.2	70.0
299.0 - 299.7	0	706.0	42.2	0	57.6
0	9.4 - 10.8	727.8	0	1.4	98.6
0	49.0 - 51.0	720.5	0	6.9	93.1

TABLE V  
INFLAMMABILITY LIMITS FOR HYDROGEN CYANIDE - HEPTANE - AIR

Partial pressure of limit mixtures, mm. of mercury		Barometer height, mm. mercury	Vol. % HCN Mean	Vol. % Heptane Mean	Vol. % Air Mean
HCN	Heptane				
54.7 - 55.2	0	707.0	7.8	0	92.2
50.3	38.0 - 39.6	718.3	7.0	5.4	87.6
100.0	30.8 - 32.1	718.3	13.9	4.4	81.7
150.0	22.9 - 24.0	718.3	20.9	3.3	75.8
200.1	12.7 - 14.1	718.3	27.9	1.9	70.2
299.0 - 299.7	0	706.0	42.4	0	57.6

TABLE VI

INFLAMMABILITY LIMITS FOR HYDROGEN CYANIDE - METHYL CHLOROFORMATE - AIR

Partial pressure of limit mixtures, mm. mercury		Barometer height, mm. mercury	Vol. % HCN Mean	Vol. % Methyl chloro- formate	Vol. % Air Mean
HCN	Methyl chloroformate				
54.7 - 55.3	0	707.0	7.8	0	92.2
0	75.1 - 76.1	714.0	0	10.6	89.4
252.0	20.2 - 22.2	714.1	35.3	3.0	61.7
215.5	43.1 - 45.2	713.7	30.2	6.2	63.6
140.0	78.5 - 80.7	714.1	19.6	11.1	69.3
92.0 - 99.6	100.1	714.1	13.3	14.0	72.7
299.0 - 299.7	0	706.0	42.4	0	57.6
21.3	50.0 - 52.0	710.0	3.0	7.2	89.8
36.0 - 36.6	36	717.0	5.1	5.0	89.9

### Discussion

The inflammability limits for the system hydrogen cyanide - cyanogen chloride - air are plotted in Fig. 1, as the volume per cent hydrogen cyanide against volume per cent cyanogen chloride in the limit mixtures. In the

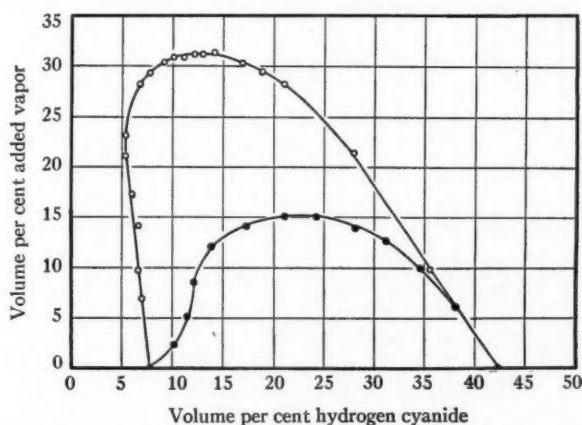


FIG. 1. Inflammability limits in the systems hydrogen cyanide - cyanogen chloride - air and hydrogen cyanide - phosgene - air.

○ Cyanogen chloride

● Phosgene

absence of cyanogen chloride, the inflammability limits are 7.8 and 42.4 volume % hydrogen cyanide. It is seen that the initial effect of the cyanogen chloride is to decrease both upper and lower inflammability limits of hydrogen cyanide, but eventually they meet. Any gas mixture with a composition

inside the area formed by the curve and the hydrogen cyanide axis will inflame under the conditions of these experiments, while any composition outside this area is noninflammable.

A given mixture of hydrogen cyanide and cyanogen chloride may or may not become inflammable when progressively diluted with air. The maximum molar ratio of cyanogen chloride to hydrogen cyanide in the mixtures which will become inflammable when so diluted is given by the slope of the line passing through the origin and tangent to the inflammability curve. The value for this ratio, found from Fig. 1, is 4.7. Mixtures of cyanogen chloride and hydrogen cyanide in which the ratio of cyanogen chloride to hydrogen cyanide is greater than this value will not pass through the inflammable region as they are progressively diluted with air, while mixtures with a molar ratio smaller than this value will become inflammable when suitably diluted. The actual amounts of air required to render such mixtures inflammable may be readily calculated using the inflammability curve of Fig. 1.

The inflammability limits in the system hydrogen cyanide - phosgene - air are also given in Fig. 1. The effect of the addition of phosgene is to bring the upper and lower inflammability limits of hydrogen cyanide together until eventually they meet. The maximum molar ratio of phosgene to hydrogen cyanide in the mixtures that pass through the inflammable region on dilution with air is found from the slope of the tangent to the curve to be 0.86.

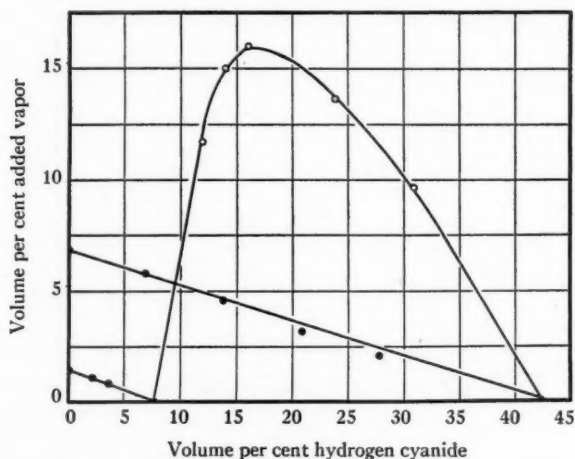


FIG. 2. Inflammability limits in the systems hydrogen cyanide - chloroform - air and hydrogen cyanide - hexane - air.

○ Chloroform

● Hexane

In Fig. 2 are presented the results on the systems hydrogen cyanide - chloroform - air and hydrogen cyanide - hexane - air. The effect of the addition of chloroform is similar to that of phosgene in that the upper and lower limits



of hydrogen cyanide approach each other and then meet as the amount of chloroform is increased. The maximum molar ratio of chloroform to hydrogen cyanide in the mixtures that become inflammable when a suitable amount of air is added is found to be 1.1.

The effect of the addition of hexane is considerably different from that of cyanogen chloride, phosgene, and chloroform, because hexane is itself inflammable. The upper and lower inflammability limits for hexane in air were found to be 6.9 volume % and 1.4 volume %, respectively. These results agree with the values 6.9% and 1.2% listed by Coward and Jones (2) for *n*-hexane. From Fig. 2, it can be seen that the compositions of the limit mixtures in the system hydrogen cyanide - hexane - air lie on straight lines joining the compositions of the corresponding limit mixtures of the binary system hydrogen cyanide - air and hexane-air. This system, therefore, follows Le Chatelier's law (6), which states that mixing upper or lower binary limit mixtures of two inflammable gases will produce an upper or lower limit mixture, respectively, of the resulting ternary system.

From Fig. 2 it is obvious that all mixtures of hexane and hydrogen cyanide, as air is progressively added, will pass through the inflammable region. Thus, all such mixtures will be rendered inflammable when suitably diluted with air.

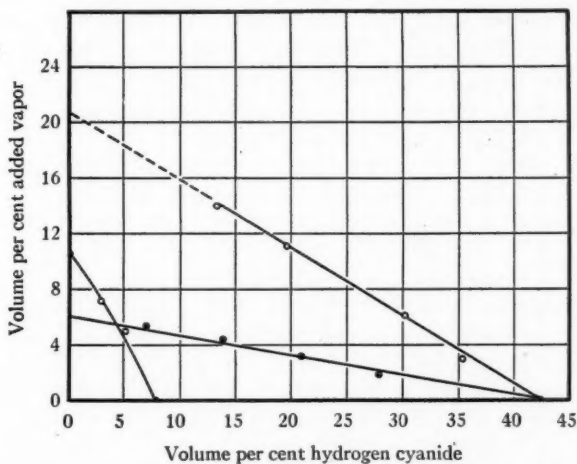


FIG. 3. Inflammability limits in the systems hydrogen cyanide - heptane - air and hydrogen cyanide - methyl chloroformate - air.

○ Methyl chloroformate      ● Heptane

In Fig. 3 is represented the effect of heptane on the upper inflammability limit of hydrogen cyanide, and also the effect of methyl chloroformate on both the upper and lower inflammability limits. These results indicate a linear decrease in the measured inflammability limits as either of these gases is added.

The lower inflammability limit of methyl chloroformate in air was found to be 10.6 volume %. The upper inflammability limit cannot be measured directly at room temperature since the vapor pressure of this material under such conditions is not sufficient to produce a noninflammable mixture with air. The saturated vapor concentration is less than the concentration in the upper limit mixture. A tentative value may be found, however, by assuming that Le Chatelier's law holds at higher concentrations of methyl chloroformate as it does for those compositions that could be measured. Extrapolation of the straight line representing the compositions of the upper limit mixtures to 0% hydrogen cyanide gives the value 20.6 volume % for the upper limit of methyl chloroformate in air.

### References

1. BOHMAN, F. E. Pests, 9 : No. 12, 8. 1941.
2. COWARD, H. F. and JONES, G. W. U.S. Bur. Mines Bull. No. 279. 1931.
3. DOUGLAS, D. E. and WINKLER, C. A. Can. J. Research, B, 25 : 381. 1947.
4. EGLOFF, G. Physical constants of hydrocarbons, Vol. 1. Reinhold Publishing Corporation, New York. 1939.
5. JORISSEN, W. P. Chem. Weekblad. 25 : 228. 1928.
6. LE CHATELIER. Ann. Mines. 19 : 388. 1891.
7. NENITZESCU, C. D. and PANA, C. Bul. soc. chim. Romania, 15 : 45. 1933. *Abstracted in Chem. Abstracts*, 28 : 73. 1934.
8. PETERS, G. and GANTER, W. Angew. Chem. 51 : 29. 1938.
9. SARTORI, M. The war gases. J. & A. Churchill Ltd., London. 1940.
10. STUSIAK, M. and SEYER, W. F. Private communication.
11. WILLARD, H. H. and FURMAN, N. H. Elementary qualitative analysis. 3rd ed. D. Van Nostrand Company, Inc., New York. 1940.

## ALUMINUM SOAPS AS HIGH POLYMERS<sup>1</sup>

BY H. SHEFFER

### Abstract

Viscosity and osmotic pressure measurements were carried out on dilute benzene solutions of aluminum dicaprylate, dilaurate, dimyristate, dipalmitate, distearate, and monostearate. From the results it is concluded that these soaps are polymers of high molecular weight formed by weak intermolecular links which are assumed to be hydrogen bonds. Lowering of the molecular weight by dissociation of these bonds is responsible for decreases in solution viscosities. Variations of the molecular weights obtained (60,000 to 900,000) are due, in the main, to the effect of concentration and aging on the extent of this dissociation.

Because of their effectiveness as thickening agents for many organic solvents, aluminum soaps have been used extensively in the manufacture of greases and in the paint and allied industries. During the recent war they were found to be the most suitable thickeners for flame-thrower fuels and incendiary bomb gels (5, 9).

The excellent gelling power of aluminum soaps is illustrated by the fact that rigid gels can be obtained with concentrations as low as 3%. With 0.3% soap solutions in benzene, relative viscosities as high as 20 have been obtained. It would thus appear that either the aluminum soaps exist as polymers of high molecular weight or that colloidal aggregates are formed in solution.

One of the most important properties of aluminum soap solutions requiring explanation is their deterioration with time. This is evidenced by a rather rapid rate of decrease of viscosity (see Fig. 1 and Table I). The effect of temperature on this rate can be illustrated by the results obtained from storage of a solution of 0.1% aluminum dilaurate in benzene. The relative viscosity of this solution started at 1.22 and dropped to the following values for samples stored for one week at different temperatures: 6° C., 1.09; 30° C., 1.17; 80° C., 1.01. The rate of decrease is lowest near room temperature and the viscosity decreases more rapidly with elevation of temperature, as might be expected. It is surprising, however, that lowering the storage temperature also increases the rate of change; an explanation for this will be offered below. Deterioration of the soap solutions is also accelerated by the presence of light, moisture, and traces of acid.

Another property of aluminum soap solutions that requires explanation is that the relative viscosity *increases* with elevation of temperature (17). As an example, the relative viscosity of one solution increased from 1.35 to 1.47 on warming from 25° to 30° C.

Commercially prepared aluminum soaps contain varying amounts of free acid and some of them dissolve fairly readily in many organic solvents. The pure soaps are, however, not very soluble in any solvent, but benzene and

<sup>1</sup> Manuscript received February 2, 1948.

Contribution from Defence Research Chemical Laboratories, Ottawa, Canada.

toluene appear to be the best. Even in these, prolonged heating is required in order to dissolve a soap. The addition of a small amount of a compound containing polar groups (particularly OH), such as alcohols, cellosolves, xylenols, etc., causes the soap to dissolve more rapidly and lowers the viscosity of the resulting solution considerably.

McBain and McClatchie (16) have shown that aluminum tri-soaps do not exist and that only the mono- and di-soaps can be prepared as pure compounds. In general, the mono- and di-soaps have very similar properties, differing in degree but not in kind. Except for one mono-stearate solution, this investigation is limited to the di-soaps and includes viscosity and osmotic pressure measurements on their dilute benzene solutions in an attempt to explain the above properties.

### Materials and Preparations

Aluminum dicaprylate, dilaurate, dimyristate, dipalmitate, and distearate were prepared from the corresponding fatty acids (Eastman Kodak, white-label) by metathesis of the potassium soap in aqueous solution with reagent-grade aluminum chloride. The precipitated soap was washed free of chloride and dried *in vacuo*, but it still contained a small amount of free fatty acid, which was then removed by extraction with dried reagent-grade acetone. Under these conditions this extraction can be stopped at the di-soap, but when small amounts of moisture are present the material may be hydrolyzed to the mono-soap or even to aluminum hydroxide. On the basis of ash values, all the di-soaps prepared in this manner gave ratios of moles of aluminum to moles of fatty acid of  $1.00 \pm 0.01 : 2$ . Two batches of aluminum dilaurate were prepared, and, although they gave the same ash values, they were found to possess different thickening properties. These will be designated as aluminum dilaurate (A) and aluminum dilaurate (B). Only one batch of each of the other soaps was made. The monostearate was prepared by a more complicated method, which will not be gone into here.

The aluminum soaps are hygroscopic to a certain extent. After being carefully dried, the soaps will pick up 0.2% moisture on short exposures, for example, while weighing. On exposure to air at about 70% relative humidity, the moisture content of the soap rises to 0.6–0.8% over long periods. The moisture pickup during weighing is not serious since this small amount of moisture is insignificant in the very dilute benzene solutions.

Solutions, varying from 0.025% to 1.0% in concentration, were made up by dissolving the required weight of soap in 600 cc. of Merck's reagent benzene. In order to ensure complete solution, the soap was stirred in the benzene under standardized conditions at the reflux temperature of the solvent for  $2\frac{1}{2}$  hr. After cooling, the solutions were filtered to remove dust particles and stored in screw-top bottles in the dark at constant temperature ( $30^\circ \pm 0.5^\circ \text{C.}$ ). Solutions prepared in this way will be termed 'starting' or 'prepared' solutions to distinguish them from those obtained by their dilution.

### Viscosity Measurements

The viscosity measurements were carried out in Ostwald-type viscometers at  $30 \pm 0.01^\circ\text{C}$ . In order to test for structural viscosity, viscometers of solvent efflux-time varying from 50 to 225 sec. were used. In all cases kinetic energy corrections were applied. It was found that the structural viscosity effect was negligible over this range for the very dilute solutions, but became appreciable for solutions in which the relative viscosity rose above 2. In general, the measurements were made in the 'faster' viscometers\* as rapid readings were desired. Ostwald and Riedel (19) measured the structural viscosity of impure aluminum soap solutions, obtaining a rapid rise in apparent viscosity at very low rates of shear, especially with the more concentrated solutions. At higher rates of shear, however, the apparent viscosity became constant.

The decrease with time of the relative viscosity ( $\eta_{\text{rel}}$ ) for solutions of aluminum dipalmitate is shown in Fig. 1. The corresponding data for

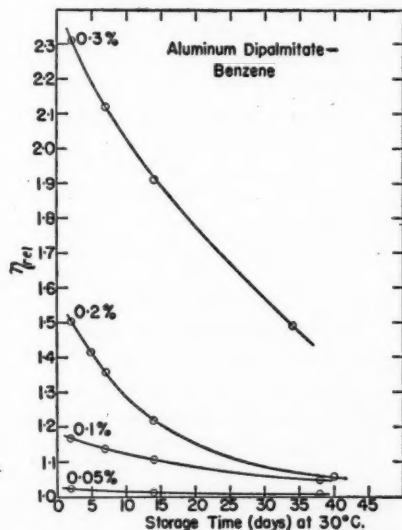


FIG. 1. Decrease in relative viscosity of aluminum dipalmitate solutions with time.

aluminum dilaurate and dicaprylate solutions are given in Table I. Because the viscosity decreases most rapidly within the first day or two after preparation of the solutions, values obtained after two days' storage are taken as the basis for comparison in this investigation.

For a high molecular weight compound dissolved in a given solvent, a value of the intrinsic viscosity (12) can be obtained, which is characteristic of the polymer in this solvent at the temperature of measurement. In order

\* Volume = 5.2 ml.; length of capillary = 11.9 cm.; radius of capillary = 0.0389 cm.

TABLE I

RATE OF DECREASE OF  $\eta_{rel}$  FOR ALUMINUM SOAP - BENZENE SOLUTIONS STORED AT 30° C.

Soap	Con- centration, gm./100 cc.	$\eta_{rel}$ after storage for					
		2 days	7 days	14 days	21 days	35 days	56 days
Aluminum dilaurate (A)	0.05	1.059	1.043	1.028	1.022	1.014	1.010
	0.10	1.224	1.186	1.149	1.120	1.074	1.033
	0.20	1.765	1.631	1.500	1.380	1.220	1.100
	0.40	4.43	3.81	3.31	2.82	2.10	1.50
	0.70	21.6	17.7	16.2	14.4	11.6	9.0
Aluminum dicaprylate	0.05	1.035	1.018	1.009	1.007	1.005	1.004
	0.12	1.266	1.130	1.059	1.038	1.022	1.009
	0.20	1.575	1.275	1.125	1.069	1.042	1.030
	0.30	3.70	2.68	2.11	1.80	1.41	1.137

to determine if a value for the intrinsic viscosity of an aluminum soap in benzene could be obtained, a 0.4% solution of aluminum dilaurate (A) was prepared and its specific viscosity ( $\eta_{sp}$ )\* measured after two days' storage at 30° C. This starting solution was then diluted to 0.3% by the addition of benzene at the same temperature and ( $\eta_{sp}$ )<sub>0.3</sub> was evaluated. Similarly, lower concentrations were prepared by dilution of the 'starting' solution. On plotting  $\eta_{sp}/c$  against concentration for these solutions, the straight line in Fig. 2 labeled 0.4% (2 days) was obtained. Extrapolation of this line gave the value of the intercept or intrinsic viscosity  $[\eta] = 3.1$ . When measurements were made on a 0.2% 'starting' solution, prepared in the same manner as the 0.4% solution, the value of ( $\eta_{sp}/c$ )<sub>0.2</sub> did not lie on this straight line as would be expected for an ordinary high polymer, but was considerably lower. Measurements on diluted solutions of the 'prepared' 0.2% solution gave points lying on a separate straight line labeled 0.2% (2 days) in Fig. 2. In this case  $[\eta] = 2.1$ . Similarly, starting with a 0.1% solution, a value of 1.65 was obtained for the intrinsic viscosity. It would thus appear that the intrinsic viscosity increases with the concentration of the 'starting' or 'prepared' solution.

The decrease of viscosity with time was often quite noticeable, even during the relatively short period required to make several check measurements in the viscometers, in which the solutions were now exposed to air and light. This decrease was found to be accelerated by the presence of acid fumes in the air. Also, when a 'prepared' solution was diluted considerably, the viscosity of the diluted solution decreased more rapidly than that of the original. In these cases several measurements were taken and an extrapolation to the time of dilution was made. These factors decrease the accuracy of the viscosity measurements so that, at the lowest values, the intrinsic viscosities may be in error by as much as  $\pm 20\%$ , while the highest values of

$$* \eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}} = \eta_{rel} - 1.$$



the intrinsic viscosities should not be in error by more than  $\pm 3\%$ . These estimates of the probable error are based on the reproducibility of measurements.

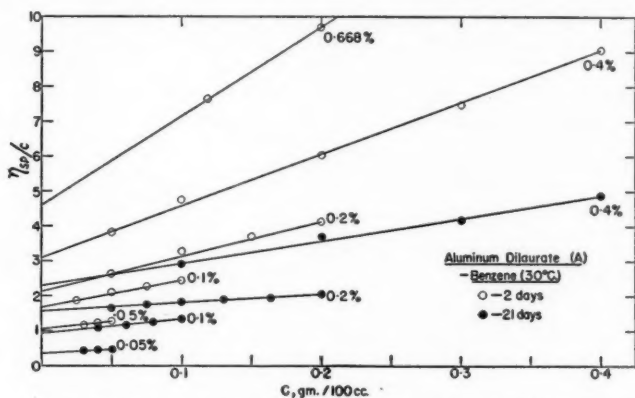


FIG. 2.  $\eta_{sp}/c$  vs.  $c$  for aluminum dilaurate (A) solutions.

The experimental viscosity results for aluminum dilaurate (A) are given in Fig. 2, those for dilaurate (B) in Fig. 3, for the dipalmitate in Fig. 4 and

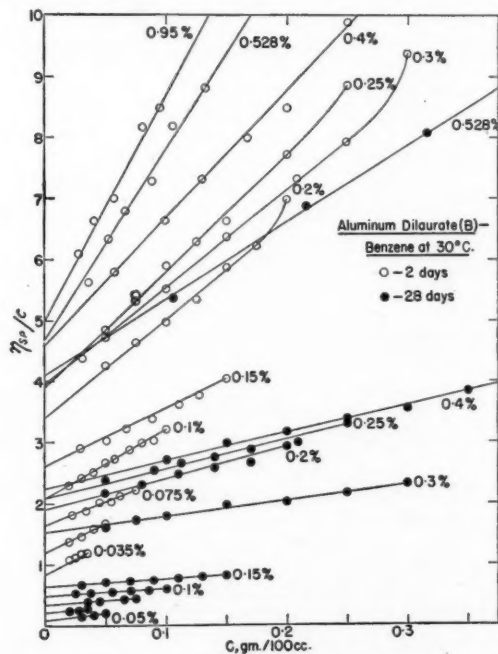
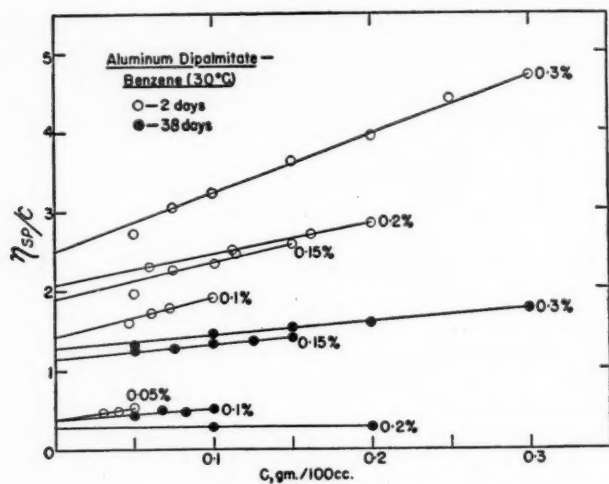


FIG. 3.  $\eta_{sp}/c$  vs.  $c$  for aluminum dilaurate (B) solutions.

FIG. 4.  $\eta_{sp}/c$  vs.  $c$  for aluminum dipalmitate solutions.

dicaprylate, dimyristate and distearate in Fig. 5. The values of the intrinsic viscosity are tabulated in Table II, together with values of the constant  $k_1$

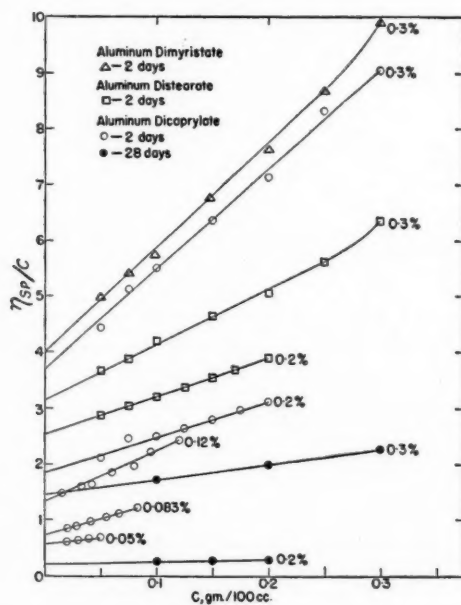
FIG. 5.  $\eta_{sp}/c$  vs.  $c$  for some aluminum soap solutions in benzene at 30° C.

TABLE II

INTRINSIC VISCOSITY-MOLECULAR WEIGHT FOR ALUMINUM SOAP - BENZENE SOLUTIONS AT 30°C

Soap	Concentration, gm./100 cc.	Storage time, days	$[\eta]$	$\left(\frac{\pi}{c}\right)_{c=0}$	$M_n$	$k_1$	$\mu_1$
Aluminum dilaurate (A)	0.05	2	1.04	1.0	295,000	4.4	0.50
		21	0.35	1.7	175,000	(19)	
	0.10	2	1.64	0.80	370,000	3.0	
		21	0.91	1.1	270,000	5.2	
	0.20	2	2.12	0.70	420,000	2.2	
		21	1.57	1.1	270,000	1.0	
	0.40	2	3.1	0.50	590,000	1.5	
		21	2.3	0.64	460,000	1.2	
	0.668	2	4.6			1.1	
Aluminum dilaurate (B)	0.025	2	0.18	2.0	147,000		0.50
	0.035	2	0.82			(20)	
		28	0.20	2.3	128,000		
	0.050	2	1.20	0.90	330,000	4.5	
		28	0.08	3.4	87,000	(40)	
	0.075	2	1.64	0.73	400,000	3.0	
		28	0.33	1.87	158,000	(10)	
	0.10	2	2.08	0.75	395,000	2.6	
		28	0.46	1.85	160,000	6.5	
	0.15	2	2.6	0.635	465,000	1.4	
		28	0.63	1.75	170,000	3.3	
	0.20	2	3.4	0.50	590,000	1.4	
		28	1.9	0.75	395,000	1.4	
	0.25	2	3.9	0.46	640,000	1.25	
		28	2.1	1.1	270,000	1.1	
	0.30	2	3.95	0.39	760,000	1.05	
		28	1.52	1.6	185,000	1.2	
	0.30 (15°C.)	2	4.7	0.37	740,000	1.05	
	0.40	2	4.6	0.335	880,000	1.0	
		28	2.25	1.36	217,000	0.9	
	0.528	2	4.7			1.4	
		28	4.1			0.8	
	0.95	2	5.0			1.4	
		28	4.5			1.0	
Aluminum dicaprylate	0.05	2	0.57			(8)	0.50
	0.083	2	0.73	2.17	136,000	(11)	
		28	0.18	4.6	64,000		
	0.12	2	1.33	1.4	210,000	5.2	0.50
		28	0.21	3.2	90,000		

TABLE II—*Concluded*  
 INTRINSIC VISCOSITY-MOLECULAR WEIGHT FOR ALUMINUM SOAP-BENZENE  
 SOLUTIONS AT 30° C.—*Concluded*

Soap	Con- centration, gm./100 cc.	Storage time, days	$[\eta]$	$\left(\frac{\pi}{c}\right)_{c=0}$	$M_n$	$k_1$	$\mu_1$
	0.20	2	1.85	1.35	220,000	1.9	0.47
		28	0.21	4.0	74,000	(9)	
	0.30	2	3.7	1.02	290,000	1.3	0.54
		28	1.45	2.5	118,000	1.3	
Aluminum dimyristate	0.075	2	1.0	1.13	260,000	(20)	
	0.15	2	2.0	0.90	330,000	4.8	
	0.30	2	4.0	0.60	490,000	1.15	0.45
	0.60	2	5.4			1.0	
Aluminum dipalmitate	0.05	2	0.38	1.8	165,000	(21)	
		38	0.10	4.4	67,000		
	0.10	2	1.42	0.9	330,000	2.4	
		38	0.4	1.9	155,000		
	0.15	2	1.9			1.25	
		38	1.15	1.6	185,000	1.2	
	0.20	2	2.07			1.0	
	38	0.28	2.8	105,000			
0.30	2	2.50	0.76	390,000	1.15	0.465	
	38	1.27	1.45	205,000	1.05	0.45	
Aluminum distearate	0.30	2	3.15	0.50	590,000	1.0	0.46
	0.20	2	2.54	0.725	410,000	1.05	0.49
Aluminum monostearate	0.30	2	2.35			1.9	

evaluated from the slope of the viscosity plots using the equation of Huggins (11):

$$\frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c.$$

The data that are most valuable for purposes of comparison are those obtained from the measurements after two days' storage. The results obtained after storage for 21 to 38 days are also included in these graphs and in Table II, and show the magnitude of the decrease in  $[\eta]$  on storage.

#### Osmotic Pressure Measurements

Osmotic pressure measurements on aluminum dilaurate solutions were carried out by McBain and Working (17) in osmometers that took two or more days to attain equilibrium, a feature that is undesirable because of the deterioration of the solutions with time. In this investigation a Fuoss-Mead (8) type of osmometer was used in order to obtain speedy results.

Collodion membranes were prepared in a manner similar to that described by Fuoss and Mead (8). After denitration and washing, the edges of the membranes were clamped between two brass rings to prevent distortion during the transfer from alcohol to benzene. The membranes were treated in succession with 50-50 alcohol-water, alcohol, 25 alcohol - 75 benzene and several changes of benzene. To obtain stable membranes it was found necessary to soak them in benzene for at least one week. Membranes prepared in this manner were found to be 'fast' enough to give static equilibrium in as little as one half-hour, so that, in general, dynamic measurements were not made except occasionally to check the static ones.

The osmometer was insulated by packing in 'rock-wool' in a box from which only the valve blocks and capillaries protruded. This box was then placed in a glass-windowed air-thermostat kept at  $30^{\circ} \pm 0.1^{\circ} \text{C}$ . The lagging prevented any appreciable fluctuations in temperature from reaching the osmometer and affecting the capillary heights. A good membrane, suitably rinsed, could be used for months, so that when the osmometer was assembled the crack between the two half-cells was sealed over with porcelain cement to prevent solvent leakage by diffusion through the edge of the membrane. This cement could easily be chipped off when it was desired to change the membrane. The solutions and solvent were kept at the same temperature as the osmometer. Measurements of the osmotic pressure were obtained using a cathetometer that read to 0.005 cm. Readings were usually taken over a two hour period in order to ensure thermal, as well as osmotic, equilibrium, since the temperature fell slightly when the door of the thermostat was opened.

No appreciable adsorption of solute by the membranes was observed, but the 'fast' membranes were somewhat permeable to solute particles below 100,000 in molecular weight. Appreciable transfer of solute occurred over 24 hr., but in most cases this was negligible over the short periods of measurement. In a few cases where the osmotic pressure was high, this transfer was more rapid and it was found necessary to extrapolate the readings back to the time of filling. For low values the osmotic pressure remained constant over periods of two to three hours, even for highly diluted 'prepared' solutions. No doubt the absence of air and light in the osmometer was responsible for the rate of deterioration being lower than that observed in the viscometers.

The experimental results for aluminum dilaurate (A) solutions are given in Fig. 6 in the plot of  $\frac{\pi}{c}$  against concentration ( $\pi$  = osmotic pressure in centimeters of benzene corrected for the difference in capillary heights with solvent in both half-cells). The line labeled 0.4% (2 days) represents a 'starting' solution of 0.4% and points obtained by dilution of this solution. The value of  $\left(\frac{\pi}{c}\right)_{0.2}$  for a 'starting' solution of 0.2% does not lie on this line, but considerably above it, and the second straight line labeled 0.2% (2 days) was obtained using the results for solutions obtained by its dilution. Similarly

a third line was derived for a 'starting' concentration of 0.1%, etc. It would thus appear that there is a different value of  $\left(\frac{\pi}{c}\right)_{c \rightarrow 0}$  for each 'starting' or 'prepared' solution, and that the apparent number average molecular weight

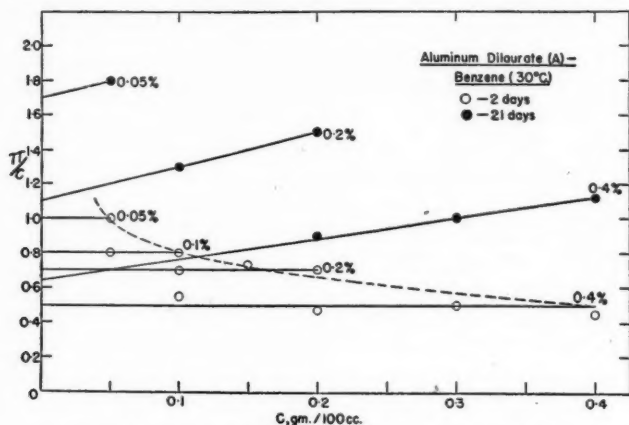


FIG. 6.  $\pi/c$  vs.  $c$  for aluminum dilaurate (A) solutions.

for the aluminum dilaurate increases with increasing concentration of these solutions.

The osmotic pressure results for aluminum dilaurate (B) are given in Fig. 7 and include a comparison between 0.3% solutions at 15°C. and 30°C.

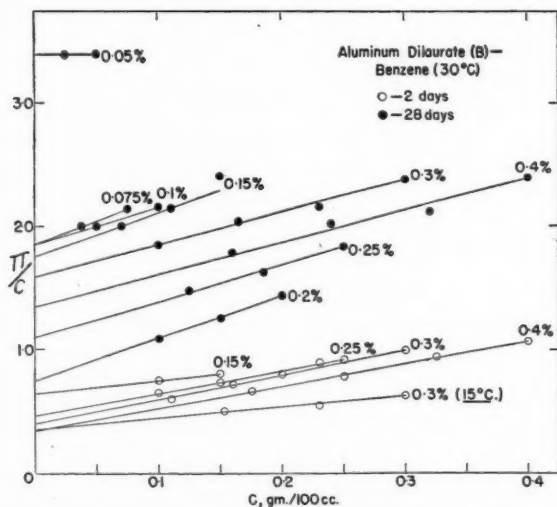


FIG. 7.  $\pi/c$  vs.  $c$  for aluminum dilaurate (B) solutions.



The results for the remaining soaps are shown in Fig. 8. The values of  $\left(\frac{\pi}{c}\right)_{c=0}$ ,  $M_n$  (number average molecular weight) and  $\mu_1$  are given in Table II.

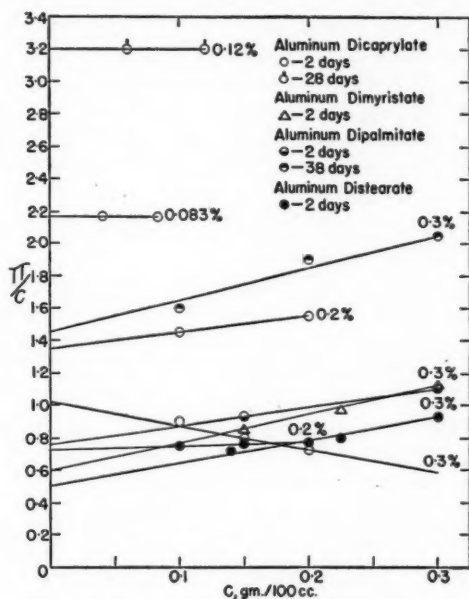


FIG. 8.  $\pi/c$  vs.  $c$  for some aluminum soap solutions in benzene at 30° C.

The latter were obtained from the  $\frac{\pi}{c}$  vs.  $c$  plots by applying the equation of Flory (6) and Huggins (10):

$$\frac{\pi}{c} = \frac{RT}{M_n} + \frac{RT}{V_1 d_2^2} \left( \frac{1}{2} - \mu_1 \right) c$$

$\bar{V}_1$  = partial molal volume of the solvent, .

$d_2$  = density of the solute (1.02 – 1.07 for the soaps from the values of Ostwald and Riedel (18) ),

$\mu_1$  = a constant for each polymer-solvent system.

Higher terms in this equation are neglected here since they are negligible in very dilute solutions.

From the data in Table II for aluminum dilaurate (A), it is seen that the molecular weights decrease to 60–75% of the '2-day' values after 21 days' storage. The corresponding decrease is to 25–40% for aluminum dilaurate (B) after 28 days, 35–40% for the dicaprylate after 28 days, and 40–55% for the dipalmitate after 38 days.

Based on reproducibility, the possible errors in the values of the higher molecular weights are of the order of  $\pm 10\%$ , while for values below 100,000 the error should not be greater than  $\pm 5\%$ .

### Discussion

If samples are removed at intervals during the heating period in the preparation of 'starting' solutions, it is found that the viscosity rises as the soap slowly dissolves, reaches a maximum in about two hours, and then decreases. This indicates two possible mechanisms. The first is that the soap in the solid state is itself a high polymer which breaks down somewhat on being put into solution and on subsequent storage. The second possibility is that the soap is a monomer which is polymerized or associated, when heated up in the solvent, to a maximum particle size which depends on the concentration.

From their osmotic pressure measurements, mentioned previously, McBain and Working (17) support the idea of association of soap molecules in solution in their conclusions: "It must be concluded that aluminum dilaurate in benzene is an association colloid whose association increases rapidly with concentration. The osmotic pressure divided by the concentration *decreases* very rapidly with concentration. This is in complete contrast with the behaviour of polymeric colloids; there the osmotic pressure divided by the concentration *increases* with concentration." It is impossible to compare the results of these authors with those of the present investigation since the preparation of solutions and time of measurements were not described. However, this conclusion is based on a curve similar in type to the dotted curve shown in Fig. 6. Each point on this curve is for a 'starting' solution, each of which contains material of different molecular weight and hence this curve should not be compared with the ordinary  $\frac{\pi}{c}$  versus  $c$  plot. Furthermore, the above conclusion is based on the wrong premise, since the slopes of  $\frac{\pi}{c}$  versus  $c$  plots for high polymers may be positive, zero, or negative, depending on the solvent and temperature (4).

In order to investigate whether the solid soap is a polymer or a monomer, a 0.6% aluminum dilaurate solution was prepared for which values of  $[\eta] = 4.4$  and  $M_n = 700,000$  were obtained. The solvent was then removed by evaporation at room temperature and the recovered soap used to make up a 0.3% solution. For this solution, values of  $[\eta] = 1.8$  and  $M_n = 350,000$  were obtained as compared with  $[\eta] = 2.7$  and  $M_n = 500,000$  for a 0.3% solution of the original soap. If the soap is a monomer that is polymerized to material of  $M_n = 700,000$  in the 0.6% 'starting' solution, there is no reason for the molecular weight to fall on further concentrating by evaporation, so that the 0.3% 'recovered' soap solution should contain material of  $M_n$  higher, if anything, than 500,000. Similarly a 'starting' solution of 0.1% ( $[\eta] = 1.65$ ;  $M_n = 370,000$ ) gave, on evaporation, material whose 0.3% solution gave  $[\eta] = 1.5$  and  $M_n = 330,000$ , instead of a higher value, which would be expected if it were due to increased polymerization or association at higher concentration.

It would thus appear that the picture of polymerizing or associating the soap molecules in solution does not conform with the facts. On the other hand, the properties of these soap-solvent systems can be accounted for by considering the aluminum soaps to be high polymers formed by comparatively weak bonds that break more readily the lower the concentration of the solution. Although the bond energies have not yet been determined, the rapid deterioration of the solutions would indicate a low energy value such as associated with hydrogen bonds. Hydrogen bonding between hydroxyl groups of neighboring molecules or between the hydroxyl group of one aluminum soap molecule and carboxyl oxygen of another are possible. Another possibility is co-ordinate bonding between aluminum and carboxyl oxygens, but these would be quite strong bonds. With three or four possible points of bonding available on each molecule, a complicated cross-linked structure seems likely for the resulting polymer.

These bonds must be formed when the soap is precipitated during its preparation. Because it is extremely difficult to duplicate the conditions of preparation exactly, the molecular weights of the soaps and their thickening powers vary from batch to batch. This explains the difference between the aluminum dilaurate (*A*) and (*B*) batches, which gave identical ash values.

Melting and slowly recrystallizing a soap under vacuum was found to produce material of extremely high molecular weight. Many additional bonds would appear to be formed during this process. The material obtained by recrystallizing aluminum dilaurate (*A*) in this manner gave a 0.3% solution ( $[\eta] = 5.5$ ), the specific viscosity of which was about six times that for the corresponding solution of the original soap.

The breaking of some of the hydrogen bonds to preferentially form bonds with the added polar groups explains the fact that small additions of polar compounds considerably reduce the viscosities of soap-hydrocarbon systems. The extent of this effect on viscosity and molecular weight is shown in Table III.

TABLE III

EFFECT OF ADDING ALCOHOL TO SOLUTIONS OF 0.3% ALUMINUM DILAURATE IN BENZENE

% Alcohol added	$[\eta]$	$\left(\frac{\pi}{c}\right)_{c=0}$	$M_n$	$k_1$	$\mu_1$
0	2.7	0.59	500,000	1.5	0.50
0.5	0.70	1.20	245,000	1.2	0.47
1.0	0.36	1.64	180,000		0.47
2.0	0.30	1.74	170,000		0.44

It was found that slight traces of acid break down the soap polymers in solution quite rapidly. When a small volume of dry hydrogen chloride gas was bubbled through a very viscous solution, the viscosity decreased to nearly that of the solvent within a minute. It is thought that the presence of minute

traces of cleaning acid adsorbed by the walls of the storage bottles accounts for the rapid deterioration of some of the samples. This is particularly the case for the higher concentrations of aluminum dilaurate (B), for which a different type of bottle was used. The breakdown caused by the acid produces more low molecular weight components which affect the number average molecular weights obtained from the osmotic pressure measurements to a greater extent than the viscosity values. Consequently, the points for badly deteriorated solutions after several weeks' storage are not included in Fig. 9.

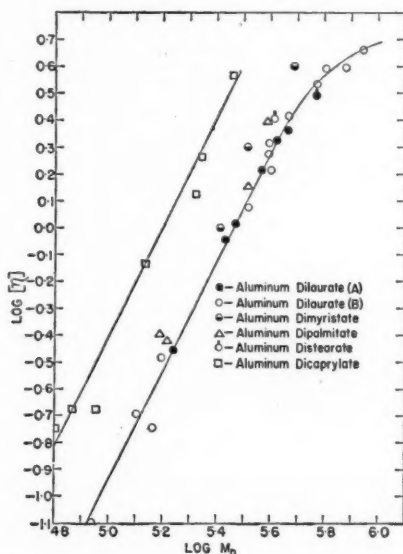


FIG. 9.  $\log [\eta]$  vs.  $\log M_n$  for aluminum soap solutions in benzene at  $30^\circ \text{C}$ .

In Fig. 9,  $\log [\eta]$  is plotted against  $\log M_n$  for solutions of all the di-soaps investigated. Curves are drawn in for the dicaprylate and dilaurate, while points for the other soaps are seen to lie relatively close to the dilaurate curve. The equation of the straight line section of the dilaurate curve was found to be  $[\eta] = 1.1 \times 10^{-11} M_n^2$ ; that for the dicaprylate is  $[\eta] = 4 \times 10^{-11} M_n^2$ . Staudinger (20) predicted  $[\eta] = KM$  for certain high polymers, but this equation was later generalized by Mark (15, p. 103) to  $[\eta] = KM^a$ . Theoretical treatments by Kuhn (14) and Huggins (11) have predicted  $a = 1$  for randomly kinked molecules and  $a = 2$  for rigidly extended rodlike molecules. Values of  $a$  below 1 occur when the molecules tend to curl more tightly. Although the exponent in the case of the soaps is found to have a value of 2, this does not necessarily indicate that the soap polymers are in the form of rigid rods in solution, since the points in Fig. 9 were obtained for solutions containing unfractionated material. Osmotic pressure measurements give number-average molecular weights that are lower for polydisperse systems

than weight-average or viscosity-average molecular weights (13). The usual methods of fractionating high polymers involve precipitation from solution by the addition of a nonsolvent (7). This is not applicable to the aluminum soaps because suitable nonsolvents are in this case polar compounds, such as alcohol, which have been shown to dissociate the linkages between soap molecules very readily. It is hoped to obtain weight-average molecular weights for these materials in the near future with the use of light-scattering measurements.

The curvature of the upper part of the aluminum dilaurate curve in Fig. 9 is analogous to that found for other polymers. In the case of cellulose acetate, Badgley and Mark (3) have attributed this effect to increased curling of the molecules of higher molecular weights.

In Fig. 10, the intrinsic viscosities are plotted against concentration in monomer units per cubic centimeter for the various soaps. Since an increase in the chain length of the fatty acid increases the effective diameter of the

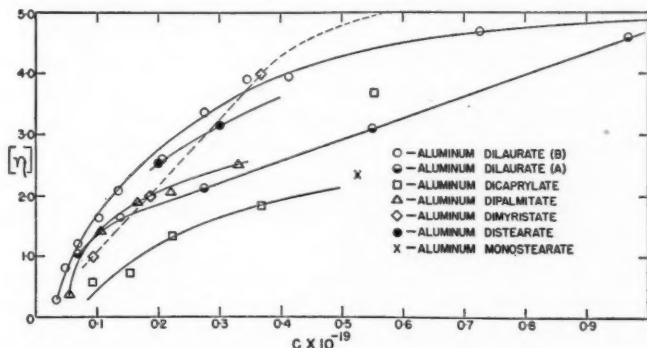


FIG. 10. Intrinsic viscosity plotted against concentration in monomer units per cubic centimeter for aluminum soaps in benzene at 30° C.

polymer, it would be expected that the viscosity at equivalent molar concentrations should increase from caprylate to stearate. In this case the same order might be expected for the intrinsic viscosities, on which the effect of structure formation would be lessened. This order is seen to hold for the dicaprylate (except for the 0.3 value which appears anomalous throughout) dilaurate (A), dipalmitate, and distearate. However, the values for the dilaurate (B) are higher than those for the distearate, while the dimyristate curve cuts across the others. This may be entirely due to variations in procedure affecting the molecular weights or it may have some real significance, as a similar effect was obtained by Ostwald and Riedel (18, 19). Again, no direct comparisons can be made, as the soaps made by these investigators contained considerable amounts of free fatty acid, the ash values lying between those for di- and tri-soaps. In their case, very low viscosity values were obtained for aluminum palmitate and stearate solutions, while the

laurate and myristate gave solutions of quite high viscosity. These authors claim that anomalous results for middle members of a homologous series are to be expected, and in this case explain them on the basis of solvation being greater in the case of laurate and myristate than for palmitate and stearate.

Considering the curve in Fig. 10 for aluminum dilaurate (*B*), which was investigated more extensively, it is seen that a limiting value of  $[\eta] = 5.0$  is approached. This corresponds to a molecular weight of about 1,000,000, which would appear to be the minimum value of the number-average molecular weight of the solid aluminum dilaurate (*B*) sample. The soap dissociates into lower molecular weight particles in dilute solutions but in more concentrated solutions and especially when gels are formed further association between molecules must take place.

Although values of  $k_1$  have usually been found to increase for solvents in which the polymers are decreasingly soluble, Alfrey (1) has pointed out that there are contradictions in the literature on this point. In Table II the values of  $k_1$  are quite high (values above 1.0 are rare in the literature) and appear to increase sharply for 'starting' concentrations below 0.1%, although the slopes of the viscosity curves cannot be measured very accurately at these low concentrations. This would indicate a fairly radical change in the internal geometry of the molecules at high dilution and might be due, in part, to an increase in the number of unassociated hydroxyl groups. However, it is not wise to speculate too much on the basis of these values, since  $k_1$  has no real thermodynamic basis.

A quantity that has much more thermodynamic meaning is  $\mu_1$ . Doty and Mishuck (4) have found that precipitation takes place in polymer solutions when the  $\mu_1$  values approach 0.55, a slightly higher figure than the critical value calculated from theory. Steep positive slopes of the  $\frac{\pi}{c}$  versus  $c$  plots and correspondingly low values of  $\mu_1$  are characteristic of systems in which the polymers are dissolved in very favorable solvents. In systems for which values of  $\mu_1$  approach 0.5, the solvents are considered to be on the borderline between nonsolvents and favorable solvents. As shown in Table II, the "2-day" values of  $\mu_1$  for all the soaps lie in the range 0.44 to 0.50, with the exception of the 0.54 figure for the anomalous 0.3% dicaprylate solution. Unfortunately, the results for the latter could not be checked, as not enough of the batch remained for preparation of a second solution. Since most of the  $\mu_1$  values are close to 0.5, benzene may be considered a relatively poor solvent for aluminum soaps.

The  $\mu_1$  data for solutions (other than dilaurate (*B*)) stored for several weeks also lie in the range 0.44 to 0.50, but in most cases the results are slightly lower than the original "2-day" values. In the case of aluminum dilaurate (*B*), the values of  $\mu_1$  have fallen to 0.40–0.42 after storage of the



solutions for four weeks. These lower values of  $\mu_1$  for the solutions which were badly deteriorated on storage are difficult to explain since it would not be expected that solvent-polymer interaction would increase under these conditions.

In more concentrated solutions an unfavorable solvent favors polymer-polymer contacts (2) or association which accounts for the formation of gel structure. In dilute solutions, the increase in relative viscosity obtained when the temperature is elevated may be explained on the basis of increased extension of the molecules as the solvent becomes more favorable with rise in temperature. In the case of the 0.3% aluminum dilaurate (*B*) solutions,  $\mu_1$  changed from 0.48 to 0.44 on elevating the temperature from 15° to 30° C. The fact that the intrinsic viscosity of the 0.3% solution at 15° C. was higher than that at 30° C. is opposite to what would be expected in an unfavorable solvent (2), but this can be accounted for on the basis of the bond dissociation being decreased by storage at 15° C.

The solutions referred to in Table III were "prepared" in the benzene-alcohol solvents rather than in benzene with the later addition of alcohol. The measurements were made after two days' storage. It is apparent that the effect of small additions of the polar compound is to make the solvent more favorable and lower  $\mu_1$ , in addition to lowering the molecular weights of the soap. A large quantity of alcohol, however, acts as a nonsolvent by precipitating the soap from solution.

That the decrease in viscosity of the solutions on storage is due to bond dissociation is evidenced by the data in Table II, which show the gradual decrease in the molecular weights of the soaps in solution. The fact that the rate of decrease of viscosity of the solutions increases with elevation of the temperature is readily explained by the corresponding increase in the rate of dissociation of the weak intermolecular bonds. On the other hand, the rapid decrease in viscosity of soap solutions at low temperatures is due to the decrease in solubility of the aluminum soap in the benzene; this results in the formation of crystallites or microcrystals. Visible crystals appear in solutions stored for long periods at low temperatures. Reheating the solutions in order to redissolve these crystals results in further bond dissociation.

An additional qualitative indication of the high-polymer nature of the aluminum soaps is the fact that they can be plasticized to give clear plastic films. By varying conditions and type of plasticizer, brittle or flexible water-repellent coatings can be made, but the mechanical strength is poor.

#### Acknowledgment

The author wishes to express his thanks to Dr. J. R. Dacey for his valued advice and criticism.

## References

1. ALFREY, T. J. Colloid Sci. 2 : 99. 1947.
2. ALFREY, T., BARTOVICS, A., and MARK, H. J. Am. Chem. Soc. 64 : 1557. 1942.
3. BADGLEY, W. J., and MARK, H. J. Phys. Colloid Chem. 51 : 58. 1947.
4. DOTY, P. and MISHUCK, E. J. Am. Chem. Soc. 69 : 1631. 1947.
5. FIESER, L. F., HARRIS, G. C., HERSHBERG, E. B., MORGANA, M., NOVELLO, F. C., and PUTNAM, S. T. Ind. Eng. Chem. 38 : 768. 1946.
6. FLORY, P. J. J. Chem. Phys. 10 : 51. 1942.
7. FLORY, P. J. J. Am. Chem. Soc. 65 : 372. 1943.
8. FUOSS, R. M. and MEAD, D. J. J. Phys. Chem. 47 : 59. 1943.
9. GREGORY, J. N. J. Council Sci. Ind. Research, 19 : 153. 1946.
10. HUGGINS, M. L. J. Phys. Chem. 46 : 151. 1942.
11. HUGGINS, M. L. *In* High polymers, Vol. 5. Cellulose and cellulose derivatives. *Edited by* Emil Ott. Interscience Publishers, Inc., New York. 1943.
12. KRAEMER, E. O. Ind. Eng. Chem. 30 : 1200. 1938.
13. KRAEMER, E. O. *In* Advances in colloid science, Vol. 2. Scientific progress in the field of rubber and synthetic elastomers. *Edited by* H. Mark and G. S. Whitby. Interscience Publishers, Inc., New York. 1946.
14. KUHN, W. Z. physik. Chem. A, 161 : 427. 1932.
15. MARK, H. Die Feste Körper. S. Hirzel, Leipzig. 1938.
16. MCBAIN, J. W. and MCCLATCHIE, W. L. J. Am. Chem. Soc. 54 : 3266. 1932.
17. MCBAIN, J. W. and WORKING, E. B. J. Phys. Colloid Chem. 51 : 974. 1947.
18. OSTWALD, W. and RIEDEL, R. Kolloid - Z. 69 : 185. 1934.
19. OSTWALD, W. and RIEDEL, R. Kolloid - Z. 70 : 67. 1935.
20. STAUDINGER, H. Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose. Verlag von Julius Springer, Berlin. 1932.

## SOLID SOLUTION FORMATION BETWEEN AMMONIUM NITRATE AND POTASSIUM NITRATE<sup>1</sup>

BY JOHN WHETSTONE

### Abstract

X-ray investigations by means of powder photographs show that solid solution formation between potassium nitrate and ammonium nitrate in simple admixture after grinding together may take place, and is considerably accelerated when the temperature is raised from ordinary temperatures to above 40° C., at which  $\text{NH}_4\text{NO}_3$  III is stable (transition temperature 32° C.). The preparation of homogeneous mixed crystals of ammonium nitrate and potassium nitrate by co-crystallization of the salts from aqueous solution is described.

### Introduction

A. N. and A. J. R. Campbell have recently reported, in an interesting paper published in this journal (1), the results of studies they have carried out on the inhibition, over as large a temperature range as possible, of the morphotropic change  $\text{NH}_4\text{NO}_3$  III  $\rightarrow$   $\text{NH}_4\text{NO}_3$  IV normally occurring at 32.3° C. The work of previous investigators of the system ammonium nitrate-potassium nitrate and of the effects of solid solution formation with potassium nitrate on the transition temperatures of ammonium nitrate, to which a number of important references were given in the paper, was extended into an investigation of the temperature limits between which the transition  $\text{NH}_4\text{NO}_3$  III  $\rightarrow$   $\text{NH}_4\text{NO}_3$  IV could be completely suppressed, either metastably or stably, by the formation of solid solutions of specified concentrations of potassium nitrate in ammonium nitrate.

The authors, however, do not appear to have had access to the important work of Jänecke, Hamacher, and Rahlfs on the systems ammonium nitrate - potassium nitrate and ammonium nitrate - potassium nitrate - water, the final results of which were given in a paper in 1932 (5). Diagrams of the phase equilibria were presented for the above systems, and the following deductions which may be made therefrom are the most helpful in understanding the nature of the solid solutions formed by ammonium nitrates III and IV with potassium nitrate.

The transition point between the modifications II and III of ammonium nitrate at 84° C. is progressively raised to a maximum of 110° C., while the transition at 32.3° C. is progressively lowered, as the percentage of potassium nitrate in solid solution with the ammonium nitrate is increased. The saturation point of potassium nitrate dissolved in ammonium nitrate IV is rapidly reached—when the content of potassium nitrate in the solid solution reaches 8% the transition temperature to the form III has been lowered to -20° C. With more than 8% of potassium nitrate the form IV is no longer a stable phase at any temperature, partial transition to form III will tend to occur

<sup>1</sup> Manuscript received in original form October 21, 1947, and, as revised, March 24, 1948.  
Contribution from the Research Department, I.C.I. Ltd., Explosives Division, Stevenston, Ayrshire, Great Britain.

with ordinary temperatures with absorption of 4.99 cal. per gm. as the heat of the transition (4), and as the potassium nitrate content is increased the equilibrium percentage of ammonium nitrate IV will decrease. At 32% of potassium nitrate, transition between forms III and V of ammonium nitrate becomes stable, and form III at normal temperatures will form solid solutions with up to about 45% of potassium nitrate. Thus a consequence of this depression of the 32° C. transition point by solid solution formation is that the solubility of potassium nitrate in the ammonium nitrate III space lattice is considerably greater than in that of the form IV of the salt.

In the conditions under which they operated, the Campbells found that "it is quite insufficient merely to mix the potassium nitrate with the ammonium nitrate: the mass must be melted up (or crystallised from solution) to produce solid solution". Work which we have carried out, however, appears to substantiate the deduction that, owing to the solubility differences, solid solution formation with potassium nitrate is likely to take place more easily with ammonium nitrate III than with the modification IV, and we have found that under certain conditions simple mixing of potassium and ammonium nitrates in the solid state does in fact result in the formation of complexes which exhibit the properties associated with solid solutions of similar composition. The evidence on which this conclusion was based was largely from X-ray crystallographic investigations by powder photographs, which are briefly described below.

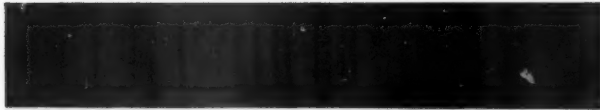
### Experimental Work

It was found that if a simple mixture of ammonium nitrate IV (either plant material several days old or B.D.H. "A.R." quality over a year old) with 10% of potassium nitrate was made by grinding for half an hour in an edge runner mill, the finely ground\* product could be used after heat treatment at 40° C. or above (which actually was combined with a drying process) in the same manner as solid solutions prepared by a fusion process. The nature of the changes taking place in this mixture was investigated by X-ray crystallographic methods. The above material when freshly prepared and before heating gave a strong X-ray powder photograph of ammonium nitrate IV (Fig. 1). On keeping for a long time at room temperatures some of the distinctive lines due to the diffraction pattern of the form III became faintly observable (Fig. 2)—probably owing to a slow progressive dissolving of potassium nitrate in the ammonium nitrate, during the aging process, tending to make the modification III the stable phase. A heat absorption of 4.99 cal. per gm. is necessary for the transition to occur (4).

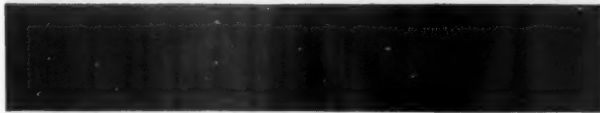
If however the milled material at 0.20% moisture content was heated overnight in an oven at 50° C., and then allowed to stand several days at room temperature, or even cooled to -20° C. for a day, the diffraction pattern had become predominantly that of ammonium nitrate III, as may be seen in Fig. 3, which appeared to be almost similar to that of a fused preparation of

\* A typical sieve analysis of milled ammonium nitrate is as follows:—Through 60 B.S.S., 92%; 100 B.S.S., 64%; 150 B.S.S., 56%; 200 B.S.S., 45%; 300 B.S.S., 36%.

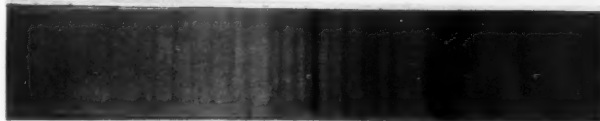
PLATE I



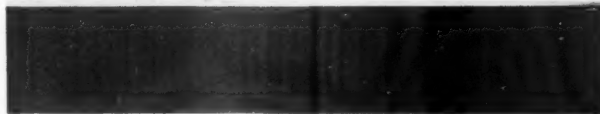
1



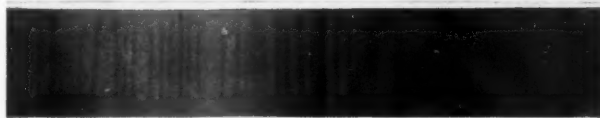
2



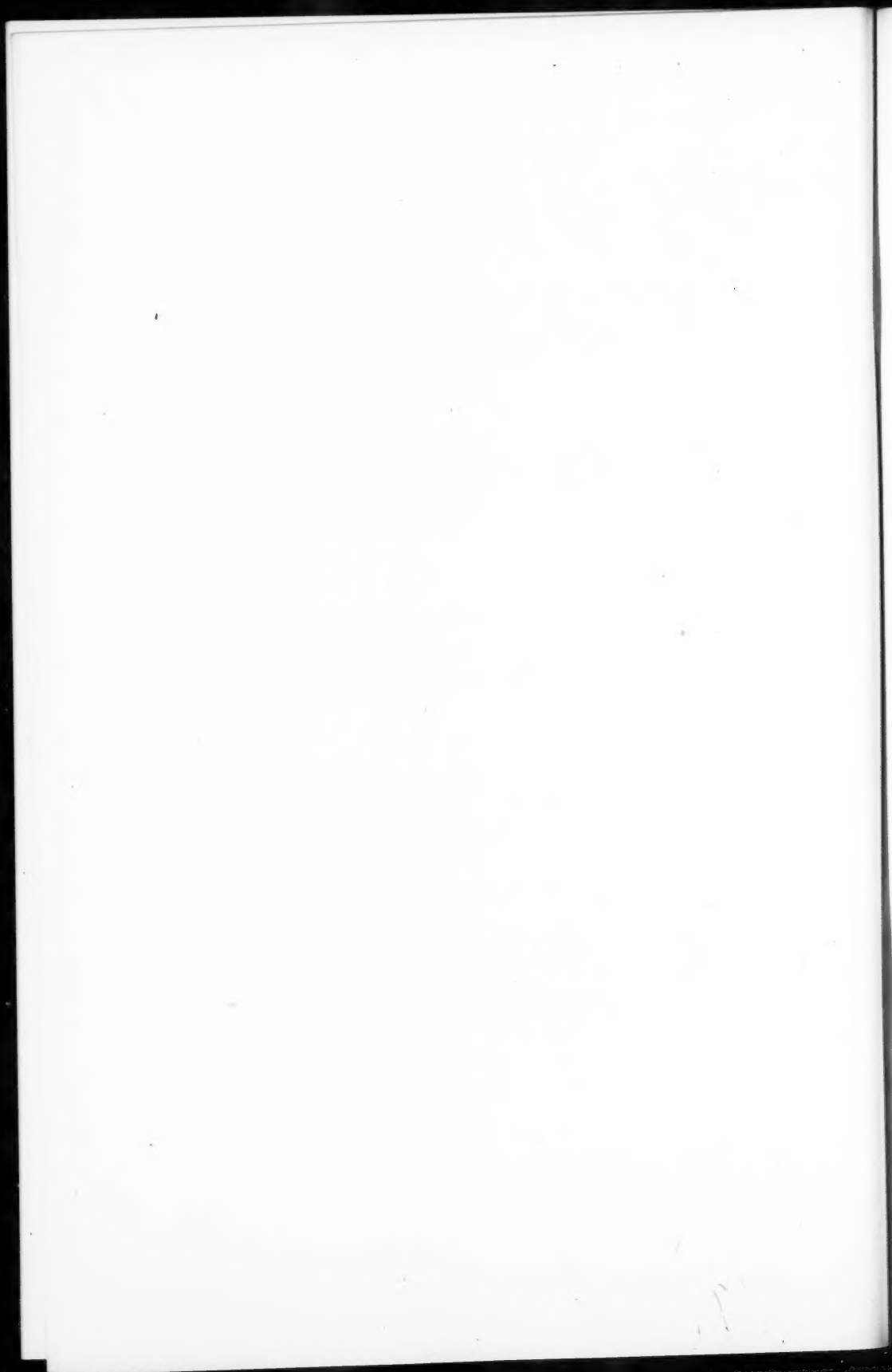
3



4



5





10% of potassium nitrate with ammonium nitrate (Fig. 5), and also to ammonium nitrate III itself (Fig. 4). It was evident that the solid solution formation had occurred very much more rapidly at 50° C. than at room temperature—a fact consistent with the greatly increased solubility of potassium nitrate in ammonium nitrate III as compared with the form IV.

There appeared to be a complete identity between the powder diffraction patterns of ammonium nitrate III (Fig. 4) and an ammonium nitrate – potassium nitrate 90 : 10 solid solution (Fig. 5) apart from a barely observable expansion in the spacing corresponding with a slight contraction of the primitive translations in the case of the solid solution. This observation was confirmed by comparing the X-ray rotation photographs of single crystals of an 81:19 ammonium nitrate – potassium nitrate solid solution, prepared according to Jänecke's data, with the corresponding rotation photographs of ammonium nitrate III crystals (2). There was no significant disparity in observed intensities between the photographs apart from the unit cell contraction in the case of the solid solution, and it was calculated that these facts were consistent with a completely random replacement of ammonium by potassium ions in the ammonium nitrate III structure.

DETAILS OF MEASUREMENTS OF UNIT CELL DIMENSIONS

Axial translation	Ammonium nitrate III at 42° C.	81:19 ammonium – potassium nitrate at 20° C.
<i>a</i>	7.14Å	7.06Å
<i>b</i>	7.67Å	7.60Å
<i>c</i>	5.84Å	5.79Å

#### *Crystallization of Homogeneous Mixed Crystals from Aqueous Solution*

Referring to the production of solid solutions of ammonium nitrate and potassium nitrate from the corresponding aqueous solutions, the work of Jänecke, Hamacher, and Rahlfs on the system ammonium nitrate – potassium nitrate – water gives a clear indication of the conditions under which homogeneous mixed crystals can be obtained. Over the temperature range 80° to 105° C. the composition of the crystals deposited is very closely parallel to the composition of the saturated solution. Outside this temperature range the disparity between the compositions is considerably increased. The only method of obtaining nearly homogeneous crops of mixed crystals involves concentrating the saturated solution at a suitable point within this temperature range.

For instance, mixed crystals containing 19.29% of potassium nitrate were prepared by crystallizing between 95° and 85° C. the saturated solution containing 80 parts of ammonium nitrate and 20 parts of potassium nitrate. The mixed crystals were of the modification III of ammonium nitrate, since the stability range is extended to 110° C. by the formation of the solid solution.

TABLE I

COMPOSITIONS OF SOLID AND LIQUID PHASES IN THE SYSTEM AMMONIUM NITRATE-POTASSIUM NITRATE-WATER BETWEEN 75° AND 105° C., ACCORDING TO JÄNECKE *et al.* (5)

Temp., °C.	Conc. $\text{NH}_4\text{NO}_3$ in mixed crystals	Conc. $\text{NH}_4\text{NO}_3$ in saturated solution	Gm. $\text{H}_2\text{O}$ per 100 gm. salt in sat'd solution
105	85.5	86.5	7.7
95	82.5	83	10
90	80.5	82	11
85	79	80	12
80	77	79	14.5
75	75.5	77.5	15

The mixed crystals were acicular, with four well developed faces of the (110) form, the interfacial angles were nearly 86° and 94°, the angle between (110) and  $(\bar{1}\bar{1}0)$  being 94°. Their refractive indices were similar to those of ammonium nitrate III (2, 3).

$$\alpha = 1.46$$

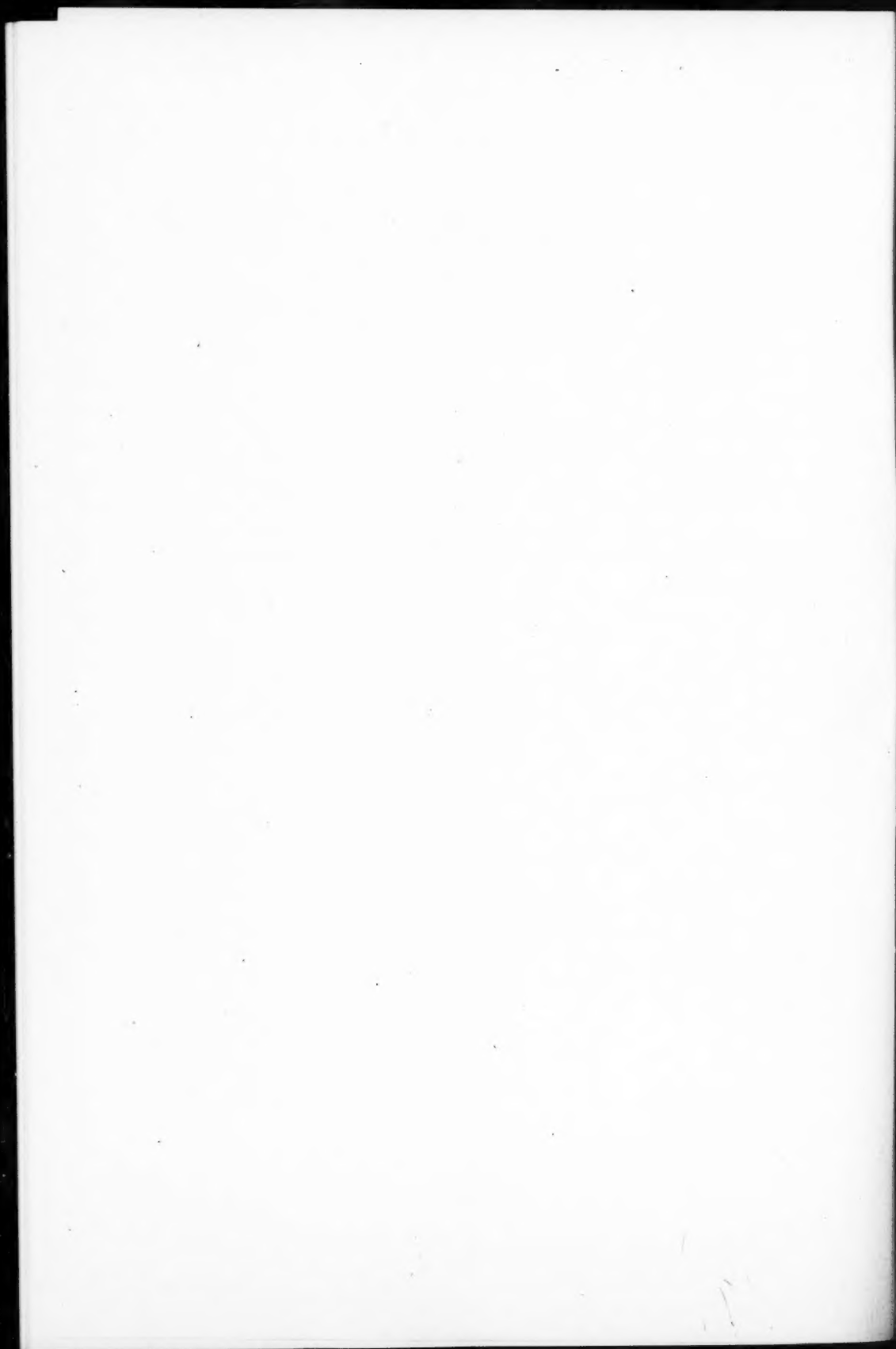
$$\beta = 1.54$$

$$\gamma = 1.60$$

#### References

1. CAMPBELL, A. N. and CAMPBELL, A. J. R. Can. J. Research, B, 24 : 93. 1946.
2. GOODWIN, T. H. and WHETSTONE, J. J. Chem. Soc. 1455. 1947.
3. HENDRICKS, S. B., DEMING, W. E., and JEFFERSON, M. E. Z. Krist. 85 : 143. 1933.
4. HENDRICKS, S. B., POSNJAK, E., and KRACEK, F. C. J. Am. Chem. Soc. 54 : 2766. 1932.
5. JÄNECKE, E., HAMACHER, H., and RAHLFS, E. Z. anorg. allgem. Chem. 206 : 357. 1932.





## CANADIAN JOURNAL OF RESEARCH

### Notes on the Preparation of Copy

**GENERAL:**—Manuscripts should be typewritten, double spaced, and the original and one extra copy submitted. Style, arrangement, spelling, and abbreviations should conform to the usage of this Journal. Names of all simple compounds, rather than their formulae, should be used in the text. Greek letters or unusual signs should be written plainly or explained by marginal notes. Superscripts and subscripts must be legible and carefully placed. Manuscripts should be carefully checked before being submitted, to reduce the need for changes after the type has been set. If authors require changes to be made after the type is set, they will be charged for changes that are considered to be excessive. All pages, whether text, figures, or tables, should be numbered.

**ABSTRACT:**—An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.

#### ILLUSTRATIONS:

(i) **Line Drawings:**—All lines should be of sufficient thickness to reproduce well. Drawings should be carefully made with India ink on white drawing paper, blue tracing linen, or co-ordinate paper ruled in blue only; any co-ordinate lines that are to appear in the reproduction should be ruled in black ink. Paper ruled in green, yellow, or red should not be used unless it is desired to have all the co-ordinate lines show. Lettering and numerals should be neatly done in India ink preferably with a stencil (do not use typewriting) and be of such size that they will be legible and not less than one millimeter in height when reproduced in a cut three inches wide. All experimental points should be carefully drawn with instruments. Illustrations need not be more than two or three times the size of the desired reproduction, but the ratio of height to width should conform with that of the type page. The original drawings and one set of small but clear photographic copies are to be submitted.

(ii) **Photographs:**—Prints should be made on glossy paper, with strong contrasts; they should be trimmed to remove all extraneous material so that essential features only are shown. Photographs should be submitted in duplicate; if they are to be reproduced in groups, one set should be so arranged and mounted on cardboard with rubber cement; the duplicate set should be unmounted.

(iii) **General:**—The author's name, title of paper, and figure number should be written in the lower left hand corner (outside the illustration proper) of the sheets on which the illustrations appear. Captions should not be written on the illustrations, but typed on a separate page of the manuscript. All figures (including each figure of the plates) should be numbered consecutively from 1 up (arabic numerals). Each figure should be referred to in the text. If authors desire to alter a cut, they will be charged for the new cut.

**TABLES:**—Titles should be given for all tables, which should be numbered in Roman numerals. Column heads should be brief and textual matter in tables confined to a minimum. Each table should be referred to in the text.

**REFERENCES:**—These should be listed alphabetically by authors' names, numbered in that order, and placed at the end of the paper. The form of literature citation should be that used in the respective sections of this Journal. Titles of papers should not be given in references listed in Sections A, B, E, and F, but must be given in references listed in Sections C and D. The first page only of the references cited in papers appearing in Sections A, B, and E should be given. All citations should be checked with the original articles. Each citation should be referred to in the text by means of the key number; in Sections C and D the author's name and the date of publication may be included with the key number if desired.

The *Canadian Journal of Research* conforms in general with the practice outlined in the *Canadian Government Editorial Style Manual*, published by the Department of Public Printing and Stationery, Ottawa.

### Reprints

Fifty reprints of each paper without covers are supplied free. Additional reprints, if required, will be supplied according to a prescribed schedule of charges. On request, covers can be furnished at cost.

